

CLOVER RESIDUE EFFECTIVENESS IN REDUCING  
ORTHOPHOSPHATE SORPTION ON FERRIC-HYDROXIDE  
COATED SOIL

By

GEORGE WILLIAM EASTERWOOD

A DISSERTATION PRESENTED TO  
THE GRADUATE SCHOOL OF THE  
UNIVERSITY OF FLORIDA  
IN PARTIAL FULFILLMENT  
OF THE REQUIREMENTS FOR THE DEGREE  
OF DOCTOR OF PHILOSOPHY

UNIVERSITY OF FLORIDA

1987

Dedicated with love to B.J.

#### ACKNOWLEDGEMENTS

With the help of various individuals, both friends and family, I was encouraged to pursue a doctoral degree. They directed me in obtaining the best education possible, and guided me to a more fulfilled life, both philosophically and intellectually.

I am deeply indebted to Dr. J. B. Sartain, my major professor, who painstakingly helped mold me intellectually. He shared with me his values, work ethic, and extensive knowledge as professor and friend. I am very fortunate to have a Supervisory Committee of scientists who display avant garde concepts. Dr. J. G. A. Fiskell, Dr. J. J. Street, Dr. E. A. Hanlon, Dr. W. G. Harris, and Dr. S. H. West are men of enlightenment and inspiration. In my opinion, I have had a Supervisory Committee that excelled in knowledge, guidance, and helpfulness. I am sincerely grateful to these gentlemen for their help and accessibility despite rigorous schedules.

I truly thank my mother and father for their encouragement in pursuing the doctoral degree. My parents, who so long ago gave me gifts of direction, self discipline, and character development by

emulation, anchored by a spirit of love, aided me more than they will ever know.

During the third year of my pursuit of a doctorate, I endured a bitter disappointment that almost devastated me. Miss Betty Jean (B.J.) Cross, my former fiancée, passed from this life. She endured the rigors of graduate school with me and was always supportive. This beautiful lady, both physically and spiritually, shall always be in my memory. It is to her, that this work is dedicated.

## TABLE OF CONTENTS

ACKNOWLEDGMENTS.....	iii
ABSTRACT.....	vii
CHAPTERS	
I INTRODUCTION.....	1
II LITERATURE REVIEW.....	4
Effect of Iron Oxides on Soil Chemical Properties.....	4
Present Management Practices for Reduction of P Fixation.....	9
Decompositional Products of Organic Materials.....	13
Organic Anion and Iron Mineral Interactions.....	17
Organo-Mineral Reactions Affecting P Fixation.....	20
III ORGANIC ADSORPTION EXPERIMENT.....	25
Introduction.....	25
Materials and Methods.....	26
Results and Discussion.....	33
Conclusions.....	45
IV PHOSPHATE AND ORGANIC AMENDMENT EXPERIMENT..	50
Introduction.....	50
Materials.....	51
Methods.....	52
Incubation Study.....	52
Glasshouse Study.....	52
Surface Charge.....	55
SEM Study.....	56
Results and Discussion.....	56
Incubation Study.....	56
Glasshouse Study.....	65
Surface Charge.....	111
SEM Study.....	118
Conclusions.....	121

V	FERTILIZER COATING AND PLACEMENT EXPERIMENT.	125
	Introduction.....	125
	Materials and Methods.....	126
	Results and Discussion.....	129
	Conclusions.....	140
VI	SUMMARY AND CONCLUSIONS.....	145
	BIBLIOGRAPHY.....	148
	BIOGRAPHICAL SKETCH.....	155

Abstract of Dissertation Presented to the Graduate  
School of the University of Florida in Partial  
Fulfillment of the Requirements for the Degree of  
Doctor of Philosophy

CLOVER RESIDUE EFFECTIVENESS IN REDUCING  
ORTHOPHOSPHATE SORPTION ON FERRIC-HYDROXIDE  
COATED SOIL

By

GEORGE WILLIAM EASTERWOOD

August, 1987

Chairman: Dr. J. B. Sartain

Major Department: Soil Science Department

Laboratory research suggests that organic acids bind to iron-mineral surfaces, reducing P fixation. Experiments were conducted to determine 1) maximal clover residue adsorption, 2) P fixation capacity of  $\text{Fe}(\text{OH})_3$  treated topsoil and goethite coated subsoil amended with clover, 3) clover residue effectiveness in relation to maize yield and extractable P levels, and 4) surface charge with P, clover, and P and clover applications to  $\text{Fe}(\text{OH})_3$  treated soils.

Amorphous iron-hydroxide ( $\text{Fe}(\text{OH})_3$ ) precipitate was applied to Orangeburg soil (fine, loamy, siliceous, thermic Typic Paleudult) at rates of 0 and 5.6 g Fe as  $\text{Fe}(\text{OH})_3$ . White clover (Trifolium repens) was grown hydroponically in Hoagland's solution.

Maximum clover residue adsorption occurred at pH 6.3 with  $\text{Fe}(\text{OH})_3$  addition. Without  $\text{Fe}(\text{OH})_3$  application, adsorption was dependent on solution ionic strength.

Clover applications decreased P adsorption within each sampling time (30, 60, 90 d) for Orangeburg soil with synthetic  $\text{Fe}(\text{OH})_3$  and Orangeburg subsoil containing goethite but increased P fixation without  $\text{Fe}(\text{OH})_3$  application.

A glasshouse experiment was conducted to measure maize yield, P uptake and extractable P levels. Two crops of maize were grown 50 d each prior to P re-fertilization for the third crop. An increase of 350% in maize yield with increases in P uptake and extractable P levels was observed with clover and P applications compared to P fertilization only, on  $\text{Fe}(\text{OH})_3$  treated soils within cropping periods. A second experiment was conducted to determine effectiveness of coating diammonium phosphate (DAP) with clover to reduce P fixation around fertilizer microsites. Point placement of fertilizer and granules was superior to mixing fertilizer and clover to soil as measured by yield, P uptake, and extractable P levels. Granules were superior to point placement in increasing P uptake and extractable P levels on Orangeburg +  $\text{Fe}(\text{OH})_3$  soil.



Surface charge studies indicated negative shifts in Zero Point of Charge (ZPC) with P and clover applications. A ZPC of 4.7, the pK of carboxyl groups, was observed with clover addition. Mechanisms of ionic complexation by organic functional groups and organic ligand exchange appeared to exist from these observations. Experimental observations indicate that applications of clover to  $\text{Fe}(\text{OH})_3$  treated soils enhanced crop production.

## CHAPTER I INTRODUCTION

In the soil environment, chemical processes favor equilibrium status of minerals although equilibrium is seldom obtained (Kittrick, 1977). Rain, however, dilutes the soil solution and promotes dissolution of mineral phases thereby increasing the soil solution activity of certain ionic species. Partial desorption of ions bound to the exchange complex also buffers the soil system. Conversely, drought may increase soil-solution ionic concentration until it is supersaturated, resulting in precipitation of a solid phase. Changes within the soil chemical environment can promote mineralogical transformations. Each of these processes, as described by Lindsay (1979), over time produce minerals possessing greater resistance to weathering. Iron-oxide formation is indicative of highly-weathered soils (Schwertmann and Taylor, 1977). Iron oxide or hydroxide minerals may exist as an independent solid phase in soils where sufficient Fe oxide concentrations exist or occur in association with the clay fraction (Carroll, 1958). In either case, iron oxides could effect surface chemistry by coating clay minerals (Stevensen, 1982).

Phosphorus (P) fixation, which is reduction of soil solution phosphate by Fe minerals, may occur by adsorption to the solid phase or precipitation reactions from the solubility products (Chu et al., 1962). Adsorption may occur as a mono- or binuclear covalent bonding to the Fe mineral (Hingston et al., 1974). Binuclear adsorption is irreversible in that desorption is negligible. Iron ionic species may reduce P availability below pH 5.5 through precipitation reactions. If the solution species of Fe and  $\text{H}_2\text{PO}_4^-$  reach saturation with respect to the solubility product of strengite ( $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ ), precipitation can result (Lindsay, 1979).

Present management practices for reduction of P fixation include either P as an amendment, or use of a low input strategy which includes proper placement, less costly P sources, and soil amendments such as lime or silicates (Sanchez and Uehara, 1980). Another management practice that could possibly reduce P fixation would be to apply an organic amendment to the soil. Humic and fulvic acids covalently bind to Fe mineral surfaces (Parfitt et al., 1977) and reduce net positive charge (Moshi et al., 1974). Complexation of solution Fe or Al may occur by bonding ionically to the organic functional groups (Deb and Datta, 1967).

Less costly management practices of applying crop residue possibly could substantially increase agronomic

yield on high P-fixing soils. To test this hypothesis experimental objectives are 1) to assess the effectiveness of organic amendment on  $\text{Fe}(\text{OH})_3$ -treated soil which can be measured by dry-matter yield, P uptake, and extractable P levels.

2) to determine the effectiveness of organic coating on fertilizer phosphate granules in relation to dry matter yield, P uptake, and extractable P levels.

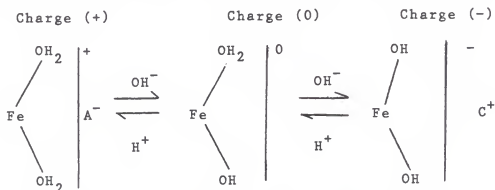
## CHAPTER II LITERATURE REVIEW

### Effect of Iron Oxides on Soil Chemical Properties

Iron oxides can exist as independent minerals in soils where significant concentrations of these oxides have accumulated (Schwertmann, 1959), or can occur in association with the clay fraction (Carroll, 1958). Follett (1965) studied the retention of amorphous ferric hydroxide in association with kaolinite, quartz, and gibbsite. He observed that the amorphous material reacted immediately with kaolinite on basal plane surfaces. Smaller amounts of amorphous ferric hydroxide were adsorbed on finely ground quartz and an insignificant amount to gibbsite. At the experimental pH of 5, which would create a net positive charge on the amorphous colloid, adsorption to negatively charged kaolinite could occur. If ferric hydroxides existed in sufficient amounts to coat soil particles, the surface chemical properties would approach that of the ferric hydroxide (Stevensen, 1982).

### Surface Charge of Iron Oxides

Surface charge of Fe oxides is pH dependent as shown in the following model (Parks and deBruyn, 1962):



Adsorption or desorption of  $\text{H}^+$  creates either a positive, neutral or negative charge on the oxide surface. As a pH-dependent charge is developed, an anion or cation ( $\text{A}^-$  or  $\text{C}^+$  ion model) is attracted to and satisfies the electrostatic charge according to the law of electroneutrality in the outer diffuse electric double layer. This type of adsorption is termed non-specific adsorption or ionic bonding (Schwertmann and Taylor, 1977).

A stronger adsorption bond is produced when ions penetrate the coordination shell of the Fe atom on the oxide surface and exchange their  $\text{OH}^-$  and  $\text{OH}_2^0$  ligands. A covalent bond is produced between the anion and oxide and is termed specific adsorption (Stevensen, 1982).

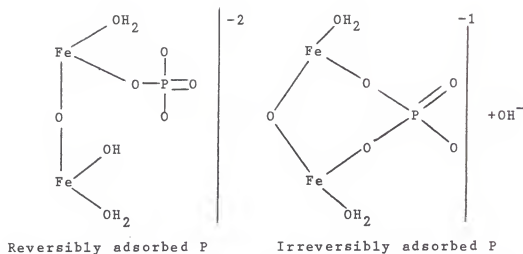
### Phosphate Fixation by Iron Oxides

Soils rich in Fe oxides, such as some Udisols and Oxisols of the tropics, are known for their low availability of phosphate (Kamprath, 1967; Fox and Kamprath,

1970). In most cases, high P content is associated with high Fe content in the soil such that Fe minerals are thermodynamically sinks for P (Taylor and Schwertmann, 1974).

Mechanisms of P fixation by Fe oxides are by precipitation and/or adsorption reactions (Chu et al., 1962). Under acidic soil conditions, the ionic activities of solution species of Fe and  $\text{H}_2\text{PO}_4^-$  may reach saturation with respect to the solubility product of strengite ( $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ ) (Lindsay, 1979). Concurrently, precipitation of strengite at low pH would occur (Lindsay and Moreno, 1960). Progressively less phosphate is precipitated as the pH is increased (Struthers and Sieling, 1950).

Specific adsorption of phosphate is another mechanism of reducing plant-available P. Hingston et al. (1974) found differences in surface-charge values of goethite after phosphate addition while measuring P adsorption. They postulated that the difference in charge was due to either mononuclear or binuclear adsorption of phosphate as shown in the following schematic:



Wann and Uehara (1978) determined that phosphate addition to Fe-oxide-rich Oxisols lowered the ZPC and increased surface charge density at any pH above the ZPC. They suggested phosphate as an amendment to increase cation exchange capacity. Parfitt et al. (1975) confirmed the binuclear coordination of phosphate adsorption in goethite using infrared spectroscopic analysis. Increasing surface area of major soil Fe oxides was observed in which amorphous ferric hydroxide > lepidocrocite > goethite > hematite. Phosphorus adsorption also increased with increasing mineral surface area.

### Kinetics

Hsu (1965) studied phosphate fixation with soils possessing Fe and Al oxides. He observed a two-stage reaction rate in which P was fixed rapidly within a few minutes or hours and a slower rate with increasing time. Adsorption of P to Fe oxides is postulated to be



a first order relationship after 48 hours of reaction time (Ryden et al., 1977) such as:

$$\frac{[A]}{t} = K[A]$$

when A, t, and K represent phosphate concentrations, time, and a constant, respectively (Bohn et al., 1985). Differences in reaction rates were attributed to mineral and solution Fe and Al (Hsu, 1965). He also stated that in principle, there was no difference between precipitation and adsorption reactions. He noted that whether a  $\text{Fe}_6(\text{OH})_{12}(\text{H}_2\text{PO}_4)_6$  or  $\text{Fe}_{54}(\text{OH})_{144}(\text{H}_2\text{PO}_4)_{18}$  compound is formed is irrelevant since the chemical reaction is the same.

Desorption is also an extremely complex phenomenon. If the enthalpies of the mononuclear and binuclear Fe phosphate complexes are similar, the binuclear adsorption would exhibit greater stability (Hingston et al., 1974) due to an increase in entropy (Martell and Calvin, 1952). Slow release of phosphate from Fe oxides has been attributed to a ring-forming, binuclear phosphate adsorption (Atkinson et al., 1972).

Phosphorus Fixation by Organic Components

During the decomposition of organic materials in acidic soils, organic functional groups can form a stable complex with Fe or Al in solution (Deb and Datta, 1967). Humic acids extracted from acid soils usually have a high Al and Fe content (Greenland,

1965). Phosphate adsorption may occur on organic material by cation bridging to Fe and Al. Bloom (1981) determined that P is strongly adsorbed by Al-saturated peat within the pH range of 3.2 to 6.0. He postulated that the mechanism of fixation was an adsorption of orthophosphate to trivalent complexed Al followed by the precipitation of amorphous Al-hydroxy-phosphate such as  $\text{Al}(\text{OH})_2 \cdot \text{H}_2\text{PO}_4$ . The strength of phosphate adsorption by this mechanism was less than that for an Al-permanent charge resin but greater than that on a weight basis of organic matter obtained from an Andept soil.

#### Present Management Practices for Reduction of P Fixation

There are at present two management alternatives for favorable P fertility on acidic soils (Sanchez and Uehara, 1980). One is a high input strategy utilizing P as an amendment and the other is a more economical low input strategy. Each method will be discussed.

#### Phosphorus as an Amendment

Fox and Kamprath (1970) determined that 95% of the maximum yield could be obtained when the fertilizer rate was adjusted such that 0.2 ug P/ml existed in the soil solution as determined by adsorption isotherms on acidic soils. To obtain that concentration, 700 kg P/ha were added. Ten y after the initial experiment, the residual efficiency which is fertilizer P effectiveness in crop production over time, ranged from

28 to 50%. It was noted that soil properties affected the residual effectiveness. Kamprath (1967) found that previously applied high rates of P fertilizer on oxisols resulted in increased yield 9 y later and that supplemental P application greatly increased yield.

Fox and Kamprath (1970) also determined that the P fixation capacity of acidic soils was reduced by high rates of initial P applications. It took less application of P, with increasing rates of initial P application, to maintain 0.2  $\mu\text{g P/ml}$  in the soil solution after 10 y.

An increase in cation exchange capacity (CEC) was accomplished by phosphate addition. As stated previously, adsorption of phosphate to Fe-oxide-coated soils increased the net negative charge of the colloid and thereby the CEC (Wann and Uehara, 1978).

High applications of P may also increase the soil pH. In acidic soils, soil-solution Al and Fe may be precipitated, thus reducing their activity (Lindsay, 1979). Stoop (1974) observed that ammonium phosphate addition increased acidic soil pH due to a decrease in anion exchange capacity.

#### Low Input Strategy

An alternative to the costly applications of massive rates of P would be the low input strategy of increased P fertilization efficiency by improving placement, using cheaper sources of P, and decreasing P

fixation through various amendments (Sanchez and Uehara, 1980).

#### Placement

Placement of fertilizer P can have an effect on yield. Kamprath (1967) obtained similar yields of maize by banding 22 kg P/ha for 7 y (154 kg P/ha) as compared with an initial application of 350 kg P/ha. Yost et al. (1979) observed that banding was inferior to broadcast applications to a high-P fixing Oxisol in Brazil, with very low levels of extractable P. The best methodology for high P fixing soils probably is an initial broadcast of P fertilizer with small annual bandings of P fertilizer (Sanchez and Uehara, 1980).

#### P Sources

Lower cost phosphate fertilizers such as phosphate rock may substitute for higher cost more soluble phosphate sources. Reactivity, as determined by the absolute citrate solubility (Lehr and McClellan, 1972) of the rock source, determines its effectiveness on acidic soils. The initial relative agronomic effectiveness of rock sources as compared to soluble superphosphate was observed by Hammond (1978) to be 79 to 94% for high, 41 to 65% for medium and 27 to 40% for low reactivity rock sources. He also observed an increase in the calculated relative agronomic effectiveness values for rock sources during subsequent cropping resulting from the slow-release characteristics of the source. Phosphate

rock may also produce a liming effect when there is a slow-carbonate release from highly-reactive rock (Easterwood, 1982).

#### Soil Amendments

Soil amendments may aid in reducing P fixation. The addition of lime reduced P fixation as measured by adsorption isotherms of Oxisols (Mendez and Kamprath, 1978), Ultisols (Woodruff and Kamprath, 1965), and Andepts (Truong et al., 1974). The pH of these soils was below pH 5.2 initially. With an increase in soil pH, the soil-solution Fe and Al activity was reduced (Lindsay, 1979). Although liming may reduce P fixation, the orthophosphate adsorption mechanism can still be operable (Parfitt et al., 1975).

Addition of silicate salts may also reduce P fixation. The silicate anion may replace phosphate on oxide surfaces (Silva, 1971). Roy et al. (1971) observed a decrease of 47% in P fixation on an Ultisol, 41% on an Oxisol, and 9% on an Inceptisol when 500 mg Si kg<sup>-1</sup> as calcium silicate was added to these soil oxides.

Another management practice that could possibly reduce P fixation is the addition of organic matter to soils. Sanchez and Uehara (1980) state that organic radicles could block exposed hydroxyls on surfaces of Fe and Al oxides. They noted that topsoils with the

same mineralogy as subsoils fix considerably less P due to the organic content in the topsoil.

#### Decomposition Products of Organic Materials

A synopsis of previous research of the chemical nature of soil organic compounds was compiled by Greenland (1965). Component properties of the humic-acid, fulvic-acid, and humin fractions were obtained from his publication and are reported below.

#### Humic Acids

Humic acids are composed of amino acids and phenolic compounds combined to form high molecular weight polymers (20,000 to 30,000). This component of organic matter is soluble in alkali and precipitated by acids. Research data indicate that humic acids at low pH have a spherical configuration. As the pH of the environment around the polymer is increased, the molecular compound increases in charge and becomes more flattened due to reduction in H bonding. Titration curves indicate a large number of acidic groups, of which about half possess a negative charge in the pH range of 5.0 to 7.0.

#### Fulvic Acids

Fulvic acids are more heterogenous than humic acids. Fractionation of fulvic acids reveals that the principle components are phenolic materials similar to humic acids but with lower molecular weight. Up to 30% of the fulvic acid may consist of polysaccharides which

also may form polymers. Polymers appear to be large, linear, flexible molecules having less carboxyl groups than in humic acids.

#### Humins

Humins are organic compounds which are irreversibly bound to the mineral part of the soil. It appears that humins have a lower carbon content compared to humic acids possibly from less aromatic compounds adsorbed to the mineral surface. These compounds appear to possess resistance against microbial degradation.

#### Clover Humification: Rate, Products, and Functional Groups

To assess the humification process, the degradation of clover (Trifolium repens) will be discussed. Topics of discussion for this section were obtained from Kononava (1966).

Plant residue decomposition is accomplished by a variety of soil microorganisms whose speciation depends on the chemical composition of the plants and soil environmental conditions. Microbes oxidize the plant material which loses its stability resulting in a decrease in weight and volume. During humification, plant residues became brown in color and, if enough water is present, an aqueous solution of humic substances may be formed.

### Rate of Decomposition

First signs of humification of clover leaves appear within 2 to 4 d with the first appearance of humic substances 2 wk after inoculation. The following observations were recorded:

Clover leaves. A microscopic examination of different sections of tissue humification enabled us to distinguish the following stages of humification:

1) A darkening of the leaves 3 to 4 days after the start of the experiment; this appears to be brought about the action of oxidizing enzymes in the tissues and also by the activity of mold fungi which form a weft on the leaf surfaces.

2) In the following 7 to 8 days, the development of an enormous number of different bacteria and protozoa is observed in the leaf tissues. The number of bacteria is so great that in some sections the tissues are completely filled with them. A gradual disappearance (like "dissolving") of the cell walls of the epidermis, particularly noticeable in young leaves, is observed from a microscopic examination of the leaf surface. At the same time, bacteria, found after isolation to be cellulose myxobacteria have penetrated into the interior of the epidermal cells.

3) These bacteria, which are at first colorless, later group themselves into slimy masses, become brown in color, and completely fill the cell. After some time, the bacteria mass in the cells undergoes lysis and is converted into a brown liquid which seeps out of the cell (Kononova, 1966. p.147)

Total humification of clover leaves took about 3 wk. Weight loss was 50 to 70% of the original material.



### Degradation Products

Decomposition rate is influenced by the ease of metabolism of the organic substrate and the percentage of slowly-metabolizable compounds. On a percentage basis of dry ash-free material before humification, clover leaves contained 23% organic-soluble substances (i.e. benzene-ethanol), 3% starch, 8% hemicellulose, 15% cellulose, 22% protein, and 4% lignin. After the humification reactions, the residue, expressed as a percentage of dry ash-free material, contained 16% substances extracted by organic solvent, 0% starch, 6% hemicellulose, 13% cellulose, 34% protein, and 16% lignin. Comparisons of chemical composition of humified and non-humified residues suggests that the percentage of material extracted with ethanol-benzene, starch, and cellulose decrease greatly during humification. Humus has a larger percentage of protein and lignin than non-humified clover since the previous components are easily metabolized. The most stable substance was lignin whose content decreased very little.

### Type and Distribution of Functional Groups

Clover leaves contain 57% C, 6% H, 32% O, and 5% N on a dry weight basis. Configurational arrangement of these elements into organic functional groups determines the reactivity of the compound or polymer. Humic substances formed from clover tend to be acidic in nature due to the reactivity of their functional groups

releasing  $H^+$  as the pK value is reached. On a percentage basis of dry ash-free material, plant residue contains 9% carboxylic, 8% alcoholic-OH, 6% phenolic-OH, and 3% methoxy functional groups producing the high reactivity of humified organic material.

#### Inorganic P Released From Clover Decomposition

During the decomposition of clover, inorganic phosphate may be mineralized. Lockett (1938) postulated that P was mineralized and assimilated into microbial lipids and nucleoproteins. Later P became available upon disintegration of microbial cells. He determined that, after decomposition, 59% of the total P was in organic form and 41% in inorganic form. He obtained similar results as those observed by Kononava (1961).

#### Organic Anion and Iron Mineral Interactions

Unlike cation bridging of organic anions to clays (Evans and Russell, 1959), the mechanism of humic and fulvic-acid anion bonding to Fe minerals is by specific adsorption or ligand exchange (Parfitt et al., 1977). The process is not sensitive to electrolyte concentrations, although it is sensitive to pH since the adsorption maximum inflection point occurs near the pH corresponding to the pK of the acid species, which is usually carboxylic and near pH 5.0 (Greenland, 1971). He reported a very strong bond between oxide and humic molecules since most functional groups of the organic

acid participate in the adsorption and their distribution was throughout the organic molecules. Greater surface area of the humic acid, at or above the pK value, allows stronger adsorption to the oxide.

Reduction of available functional groups may occur as cations are complexed from the soil solution (Zunino and Martin, 1977). Complexation is very effective in reducing Fe or Al in solution due to the stability of the complex (Deb and Datta, 1967). They found that the stability of the complex is so great that functional groups are rendered inactive with respect to further interactions with hydrous oxides. Bloom and McBride (1979) did research on the complexing ability of metal ions with humic acids. They observed that humic acids bind with most divalent metal ions, with the exception of  $\text{Cu}^{2+}$ , as hydrated species. Also, they observed that humic acids exhibit a strong affinity for trivalent ions. The  $\text{Al}^{3+}$  ion is likely bound to three carboxyl groups, but the case of the mono- and divalent species adsorption from solution cannot be ruled out (Bloom and McBride, 1979). Bloom (1979) observed the titration behavior of Al-saturated organic matter. He observed that, as the pH of the material is increased, the  $\text{OH}^-$  would most likely form  $\text{Al}(\text{OH})^{2+}$  on the organic-matter exchange sites. As the pH is increased until the activity of  $(\text{Al}^{3+})(\text{OH}^-)^3$  is exceeded, precipitation of amorphous  $\text{Al}(\text{OH})_3$  would be induced. Acid addition on

the other hand results in release of  $Al^{3+}$  ions into solution as  $H^+$  ions bind to functional groups at adsorption sites.

Freshly humified clover material adsorption on allophane was studied by Inoue and Wada (1968). They found that newly humified clover possessed a greater capacity for adsorption than humic substances extracted from soils. Possible inactivation of functional groups due to ion complexation was suggested as the reason for the reduction in adsorption (Greenland, 1971). Preferential adsorption of high molecular weight (1,500 to 10,000) decomposition products was observed on allophane (Inoue and Wada, 1968).

Different ideas exist in the literature concerning the stability of Fe-organo mineral complexes. Levashkevich (1966) determined that humic acids form more stable bonds with Al-hydroxide gels than with Fe-hydroxide gels which he stated had a lower capacity for adsorption. Greenland (1971) stated that a very strong bond would be formed between the oxide and humic molecule if several carboxyl or other groups participated. Schwertmann (1966) stated that the transformation of amorphous ferric hydroxide to a crystalline Fe mineral may be halted due to the bonding of organic ligands to the mineral. Schwertmann and Fischer (1973) determined that ferric-hydroxide surface area would be reduced by organic-ligand adsorption.

The following relationship was observed:

$S(m^2/g) = 76.6 - 16.4(\%C) + 9.56(\%Fe)$  where  $n=17$  and  $r=0.94$ .

This relationship suggests strong covalent bonding between Fe hydroxide and organic anions. Parfitt et al. (1977) determined that fulvic acid is adsorbed on goethite surfaces by ligand exchange at the pH of 6-6.5. Parfitt and Russell (1977) determined that mononucleate species, such as benzoate and 2,4-D, had a low-binding constant and were easily desorbed from goethite surfaces. Binuclear species such as oxalic acid were strongly adsorbed on the goethite surface. Appelt et al. (1975a) measured the adsorption of benzoate, p-OH benzoate, salicylate, and phthalate on Andept soils from Chile. They observed that monoprotic adsorption was by anion exchange whereas diprotic adsorption was by anion and ligand exchange.

#### Organo- Mineral Reactions Affecting P Fixation

##### Possible Mechanisms

Mechanisms relating to reduction in P fixation on Fe oxides by organic amendments are not clearly delineated in the literature. Singh and Jones (1976) stated that inorganic P from the decomposition of organic residues would possibly supply sufficient P to reduce P fixation such that added P would be in a stable form. They stated that an organic residue must contain at least 0.3% P, otherwise added P would be immobilized.

Conversely, Datta and Goswami (1962), utilizing  $^{32}\text{P}$  tracer techniques, came to different conclusions. The following excerpt is from their paper:

The increase in the uptake of total P was again due to a greater uptake of soil and not fertilizer P, except in red soil, where the uptake of both soil and fertilizer P increased. It is, however, expected that, though organic matter itself has contributed towards the amount of soil P, it is considered to bear very little in relation to such a large increase in total uptake (p 236).

Singh and Jones (1976) also stated that P adsorption could be lowered by blocking adsorption sites with decomposition products from organic matter. Bhat and Bouyer (1968), utilizing  $^{32}\text{P}$  studies, found that the addition of organic matter to ferruginous tropical soils lowered P-fixation capacity and isotopically-dilutable P was also greater. Initial soil pH was 6.6. Datta and Nagar (1968) using  $^{32}\text{P}$  studies determined that the uptake of fertilizer P was decreased substantially by organic addition in all their experimental soils except red soils where there was a slight increase in fertilizer P uptake rather than P uptake from organic and soil P. Initial soil pH of this red soil was also 6.6.

Datta and Nagar (1968) suggested that the mechanism of organic acid production could solubilize certain insoluble phosphates present in the soil. This explanation was given due to large amounts of soil

rather than fertilizer P uptake on all experimental soils except the red soil.

Deb and Datta (1967) stated that organic anions in acidic medium are very effective in complexing Fe and/or Al in solution. They observed reduction of Fe and Al activity preventing precipitation as insoluble phosphate compounds.

### Observations

Conclusions relating to the reduction of P fixation by organic addition by previous researchers are mixed. Appelt et al., (1975b) found that the adsorption of benzoate, p-OH benzoate, salicylate, phthalate, and humic and fulvic acids extracted from the surface soil of a Typic Dystrandepts did not block P adsorption sites on subsurface samples of that soil. Soil pH values ranged from 4.8 to 5.4. High extractable Al levels were observed. In their studies no characterization of the organic material relating to sesquioxide ash and P fixation capacity was given. Yuan (1980) studied the adsorption of phosphate and hot water-extractable soil organic matter on acidic soils and synthetic Al silicates. He found that pretreatment of organic material had no effect on an Eutrandept: a slight effect on a Haplaquod, and partial reduction of P fixation on a Paleudult. He observed that organic material adsorption was increased by an increase in the rate of material applied, but the amounts of P retained

by the soils were constant suggesting that adsorption sites for P and organic material were different.

Greenland (1971) determined that organo-mineral studies should be performed utilizing pure mineral and organic materials. He determined that previous reactions may block adsorption sites on hydrous oxides. Also, organic functional groups could be rendered inactive by metal complexation.

Nagarajah et al., (1970) evaluated the competitive adsorption of polygalacturonate (a root exudate with atomic weight of approximately 25,000) on synthetic goethite. At pH 4.0, polygalacturonate decreased phosphate adsorption by chelation of Fe or adsorption on the goethite surface as determined in their experiments. Hashimoto and Takayama (1971) reported that humic acid, nitrohumic acid, and nitrohumate salts inhibited P fixation on a synthetically prepared goethite, ferric hydroxide, and ferrous orthosilicate, but not by lepidocrocite or amorphous Fe oxide hydrate. Manojlevic (1965) conducted laboratory studies with humic acid derived from dung and manure on high-P-fixing soils. Humic acids decreased P fixation from granular superphosphate which was in contact with the soil for 4 mo. Moshi et al., (1974) measured phosphate adsorption from two profiles (one cultivated and one under forest environment) of Kikuyu red clay from Kenya. He reported that surface-adsorbed organic



components reduced the positive charge on the soil surface. They found a linear correlation ( $p > .01$ ) between increasing percentage of organics and reduction of positive charge. Phosphate adsorption at pH 5.0 was reduced by the presence of organic matter. They also observed a linear correlation ( $p > .01$ ) between a decrease of phosphate adsorption and increasing C%. Hinga (1973), also obtained similar results on Kenya soils.

## CHAPTER III ORGANIC ADSORPTION EXPERIMENT

### Introduction

The mechanisms of humic and fulvic anion bonding to Fe minerals are by specific adsorption or ligand exchange (Parfitt et al., 1977). The process is not sensitive to electrolyte concentration, although it is sensitive to pH since adsorption maximum occurs near the pH corresponding to the pK of the acid species, usually carboxylic, near pH 5.0 (Greenland, 1971). He found that a very strong bond was formed between oxides and humic molecules since most functional groups of the organic acid participated in the adsorption. Schwertmann (1966) stated that the transformation of amorphous ferric hydroxide to a more crystalline Fe mineral may be stopped due to the bonding of organic liquids to the mineral. Parfitt et al. (1977) determined that fulvic acid is adsorbed on goethite surfaces by ligand exchange within the pH range of 6 to 6.5.

The objectives for the organic adsorption experiment were as follows: 1) To determine pH for maximum clover decompositional product adsorption and 2) To determine time required for transformation of amorphous  $\text{Fe}(\text{OH})_3$  to a crystalline phase in relation to clover application.

## Materials and Methods

### Soil

An Orangeburg series soil (fine, loamy, siliceous, thermic, Typic Paleudult) was obtained from the Agricultural Research and Education Station near Quincy, FL. Two portions of the profile under forest environment were sampled. The surface soil, devoid of organic litter, was obtained corresponding to the A horizon. This sandy soil was to be the matrix for  $\text{Fe}(\text{OH})_3$  addition. Subsurface B horizon samples were obtained of the corresponding soil profile.

### Characterization

Both samples were characterized physically, mineralogically, and chemically. Particle size distribution was determined by the methodology of Day (1965) for the clay fraction and sieving to determine sand and silt fractions. Pretreatment with  $\text{H}_2\text{O}_2$  oxidized organic components.

Mineralogical characterization included identification of clay fraction minerals. Pretreatment included removal of organic matter with  $\text{H}_2\text{O}_2$  and free Fe oxides with citrate-bicarbonate-dithionite extraction (CDB). Free iron oxide and Al concentrations in CDB extracts were determined using atomic adsorption spectrophotometry (Kunze, 1965).

Chemical characterization included cation exchange capacity by the summation method as described by

Chapman 1965). Organic carbon was determined by dichromate-oxidation techniques (Walkley and Black, 1934). Soil pH was determined in a 1:1 ratio of soil to water (McLean, 1982). Phosphorus fixation was determined by methodology of Fassbender and Igue (1967) in which 5 g of soil were placed into a centrifuge bottle with 100 mL of 100 mg P/L solution. The bottle was shaken for 6 hours at 180 excursions/min. Separation between solution and solid phase was accomplished through millipore filtering (.2 u). Extracts were analyzed for P using methodology described by Murphy and Riley (1962). Results are given in Tables 3-1 and 3-2.

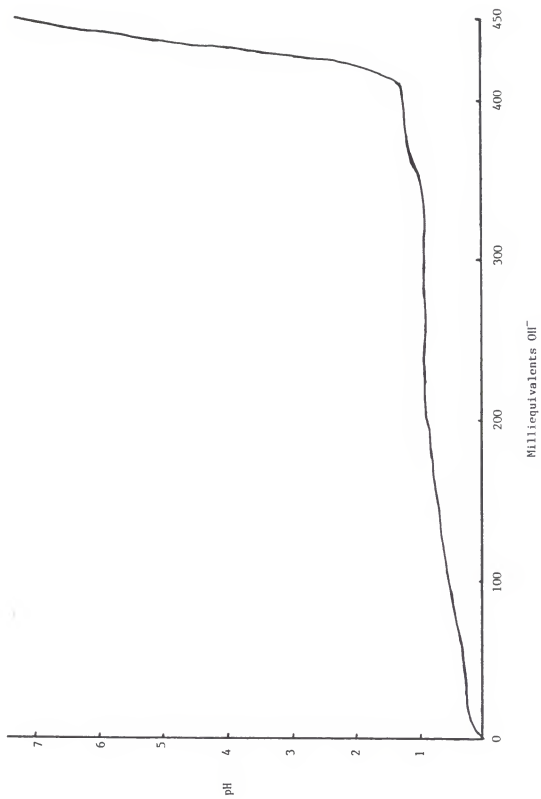
#### Fe(OH)<sub>3</sub> Synthesis

Amorphous ferric hydroxide was prepared by potentiometrically titrating 2 M Fe(NO<sub>3</sub>)<sub>3</sub> with 6 M KOH to pH 8.1 (ZPC). Equivalent concentrations of both reagents were used in precipitating the Fe(OH)<sub>3</sub> (Fig 3-1). To remove the soluble KNO<sub>3</sub> formed, approximately 2 L of deionized water was filtered through 250 g of precipitate resulting in negligible concentrations of K<sup>+</sup> and NO<sub>3</sub><sup>-</sup>. A suspension of Fe(OH)<sub>3</sub> in H<sub>2</sub>O was prepared with a concentration of approximately 1 M as Fe(OH)<sub>3</sub>. Rates of 0 and 5.6 g Fe as Fe(OH)<sub>3</sub> were applied to Orangeburg surface soil by complete mixing.





Fig. 3-1 Potentiometric Titration of 450  
Milliequivalents Fe as  $\text{Fe}(\text{NO})_3$  With KOH.





### Clover Production

White clover (Trifolium repens) was grown hydroponically to insure organic functional groups did not contain high sesquioxide ash contents. Hydroponic solution possessed ionic concentrations of  $10^{-3}$  M P,  $10^{-2.2}$  M K,  $10^{-1.8}$  M  $\text{NO}_3$ ,  $10^{-2.3}$  M Ca,  $10^{-2.7}$  M Mg,  $10^{-2.7}$  M  $\text{SO}_4$ ,  $10^{-3.5}$  M Fe, with micronutrient concentrations of 0.5 ug B/ml, 0.5 ug Mn/ml, 0.05 ug Zn/ml, and 0.02 ug Cu/ml (Hoagland and Arnon, 1938). Solutions were continually aerated and replaced biweekly. Clover biomass was harvested every 40 d and the material was then dried and ground to pass a 2- mm sieve.

### Liming Curve and Organic Adsorption Measurements

To determine the maximum organic adsorption to Orangeburg topsoil, an incubation study was initiated in which 50 g samples were treated with or without 5.6 g Fe as  $\text{Fe}(\text{OH})_3$ , plus or minus 3.15 g/kg dried and ground clover, at  $\text{CaCO}_3$  rates of 0, 0.5, 1.0, 1.5, and 2.0 cmol  $\text{CaCO}_3$ /kg soil. Reagent grade  $\text{CaCO}_3$  was mixed with soil and incubated for 2 w at 25°C and 8% moisture on a weight basis. Dried and ground clover was then applied and allowed to decompose for 30 d. Duplicate samples were prepared.

Organic anion extraction was performed by extracting 10 g of soil with 20 mL of 0.01 M NaCl and shaking for 30 min (Stevenson, 1982). Samples were centrifuged and aliquot decanted. Electrical conductivity of each

aliquot was measured prior to increase of solution pH to pH 7.0 with 0.1 M NaOH for adsorption measurements of humic and fulvic acids at 465 nm (Chen et al., 1977). Soil pH was measured in water (1:1 ratio) (McLean, 1982).

#### Crystallization of $\text{Fe}(\text{OH})_3$

Solid  $\text{Fe}(\text{OH})_3$  and  $\text{Fe}(\text{OH})_3$  associated with the clay fraction of Orangeburg soil were monitored over a 6 mo period for crystal formation. Both samples were subjected to wetting and drying cycles over time. X-ray diffraction (XRD) techniques were employed using Cu K radiation to monitor changes. Differential scanning calorimetry (DSC) techniques were also employed.

### Results and Discussion

#### Organic Adsorption Experiment

Study of organic adsorption on soil solids can produce confounding results in impure systems due to previous reactants on solid surfaces or inactivity of organic functional groups due to ion complexation (Greenland, 1971). For this reason, pure phases were prepared for study. Amorphous ferric hydroxide was applied to the Orangeburg sandy soil which was the matrix for the mineral addition. Follett (1965) observed that ferric hydroxide reacts with basal-plane surfaces of kaolinite, which is the primary clay mineral in the Orangeburg soil. Since Orangeburg soil is

acidic (pH 4.9), a liming curve after  $\text{Fe}(\text{OH})_3$  application was essential to determine pH for maximal organic adsorption. Also the pH of the soil must be greater than the dissociation constant of the organic acid (pH > 5.0) to activate organic anions (Greenland, 1971). Clover rates were similar to residue rates added to the soil for cover crop production.

Results from the incubation study with respect to treatment are given in Fig. 3-2 to 3-9. Organic adsorption relationships produced by changes in pH are given in Fig. 3-2 to 3-5 and adsorption relationships with change in ionic strength are given in Fig. 3-6 - 3-9. Numbers in parenthesis in these figures are soil pH values. Ionic strength was calculated to be the total ionic strength of solution minus the ionic strength of the 0.01 M NaCl solution. Total ionic strength was calculated by the following equation:

$$u = 0.013 \text{ EC}$$

where 0.013 is a constant and EC is electrical conductivity expressed in millimhos  $\text{cm}^{-2}$  (Griffin and Jurinak, 1973).

Stevenson (1982) stated that organic adsorption to clay surfaces was sensitive to changes in ionic strength. The mechanism of adsorption is by ionic

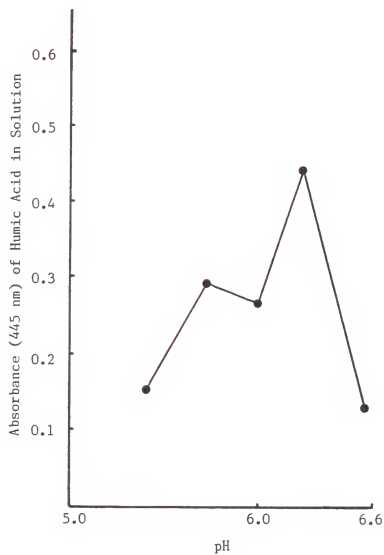


Fig. 3-2 Effect of Soil pH on Organic Release From Orangeburg Topsoil.

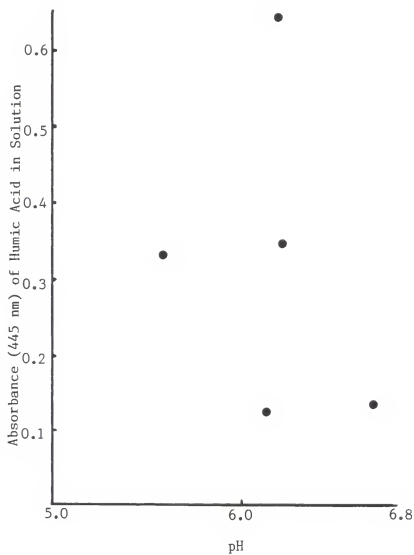


Fig. 3-3 Clover Decompositional Product Adsorption to Orangeburg Topsoil as Influenced by Soil pH.

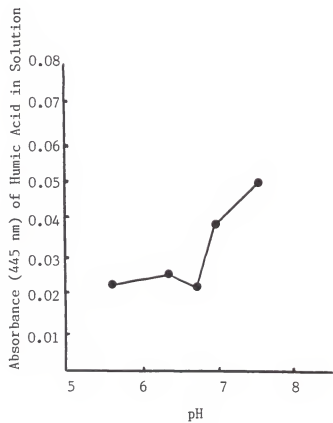


Fig. 3-4 Effect of Soil pH on Organic Release From Orangeburg Topsoil +  $\text{Fe}(\text{OH})_3$ .

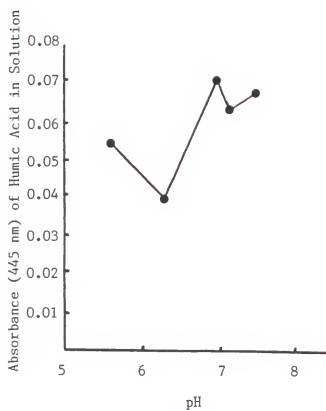


Fig. 3-5

Clover Decompositional Product Adsorption  
to Orangeburg Topsoil +  $\text{Fe}(\text{OH})_3$  as  
Influenced by Soil pH.

bonding. Similar results were obtained from the treatments of Orangeburg soil without Fe hydroxide addition. Increasing lime rates increased soil pH from 4.9 to 6.7 (Figs 3-2 and 3-3) but also increased solution ionic strength due to increased  $\text{Ca}^{2+}$  activity (Figs 3-6 and 3-7). Calcium does not form a strong complex between negatively charged clay and humic acid, but is effective as a bridge between ions (Stevenson, 1982).

Greenland (1971) observed that organic matter bound to clay through  $\text{Ca}^{2+}$  cation bridging was easily displaced by monovalent ions such as  $\text{NH}_4^+$  or  $\text{Na}^+$ . Increases in pH increase negative charges on mineral surfaces (Kaolinite) and therefore cation exchange capacity. Near pH 6.2, less organic anions were extracted by NaCl. Possibly  $\text{Na}^+$  and  $\text{Ca}^{2+}$  ions increased exchangeable  $\text{Al}^{3+}$  or  $\text{Fe}^{3+}$  levels. Aluminum and Fe at low concentrations could reduce organic anions by flocculation (Stevenson, 1982). Results are inconclusive above pH 6.2.

Stevenson (1982) also stated that organic adsorption to hydrous oxides occurred by ligand exchange or covalent bonding. Only anions that bind strongly to oxide surfaces could replace organic anions. This mechanism is insensitive to solution ionic strength but highly sensitive to pH. Salt solution extraction did not affect organic adsorption. Results in Fig. 3-4, 3-5, 3-8, and 3-9 support this mechanisms organic



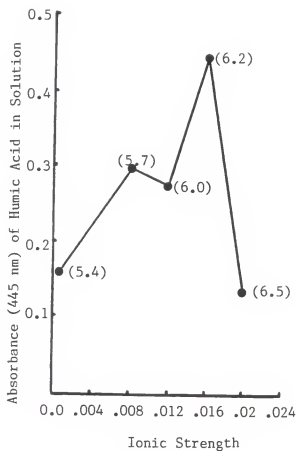


Fig. 3-6 Effect of Solution Ionic Strength on Organic Release From Orangeburg Topsoil.

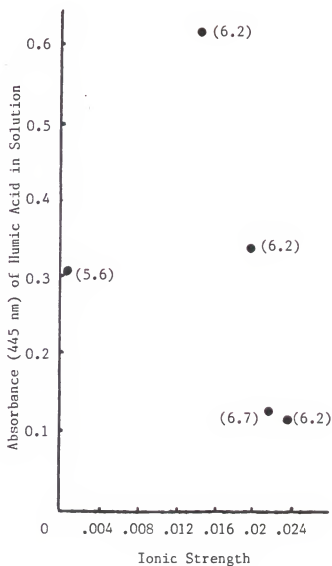


Fig. 3-7

Clover Decompositional Product Adsorption  
to Orangeburg Topsoil as Influenced by  
Solution Ionic Strength.

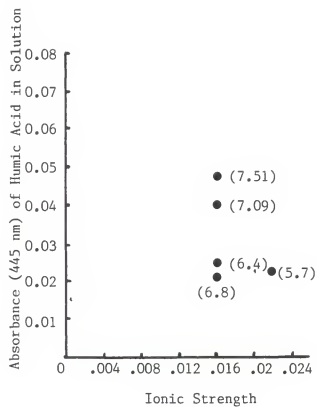


Fig. 3-8      Effect of Organic Release From Orangeburg  
Topsoil +  $\text{Fe}(\text{OH})_3$  as Influenced by  
Solution Ionic Strength.

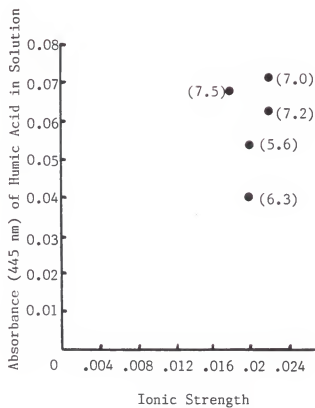


Fig. 3-9 Clover Decompositional Product Adsorption to Orangeburg Topsoil +  $\text{Fe}(\text{OH})_3$  as Influenced by Solution Ionic Strength.

covalent bonding. Organic adsorption was not affected by ionic strength as seen in Fig. 3-8 and 3-9 but was greatly affected by changes in soil pH (Fig. 3-4 and 3-5). Ionic strength ranged from 0.016 to 0.022 units whereas pH changes within small ranges of ionic strength greatly affected adsorption measurements. As pH increases above pH 5.0, organic anions are formed. However,  $\text{Fe}(\text{OH})_3$  possessed a variable charged surface so that increases in pH could reduce net positive charge and adsorption sites on mineral surface thereby resulting in reduced adsorption. Maximal organic adsorption occurred at pH 6.3 with residue amendment. It is also important to observe the effectiveness of organic adsorption of the  $\text{Fe}(\text{OH})_3$  treated soil compared to untreated soil. Several orders of magnitude of adsorption exist in the binding capacity, making the  $\text{Fe}(\text{OH})_3$ -treated soil an excellent sorbant system for organic anions.

#### Crystallization of $\text{Fe}(\text{OH})_3$

Changes in crystallization of  $\text{Fe}(\text{OH})_3$  affects surface area and reactive sites for organic anion and P adsorption. Mineralogy of solid phase  $\text{Fe}(\text{OH})_3$  and  $\text{Fe}(\text{OH})_3$  treated Orangeburg soil were observed over a 6 m period. Solid  $\text{Fe}(\text{OH})_3$  endured wetting and drying cycles whereas  $\text{Fe}(\text{OH})_3$  treated soil with and without clover amendment was under a cropping system. At no time during the 6 m period did the solid  $\text{Fe}(\text{OH})_3$

exhibit crystallinity as observed by XRD or DSC methodologies. The same result was obtained for the  $\text{Fe}(\text{OH})_3$  treated soil. Differential Scanning Calorimetric plots of Orangeberg soil +  $\text{Fe}(\text{OH})_3$  clay fractions without clover amendment and with clover amendment are given in Fig 3-10 and 3-11, respectively. No Fe mineral endotherm was observed. However, endotherms for both gibbsite and kaolinite, were observed.

### Conclusions

Adsorption study observations in conjunction with previous research suggested that  $\text{Fe}(\text{OH})_3$  treated soil exhibited covalent bonding of organic anions whereas treatments without  $\text{Fe}(\text{OH})_3$  exhibited ionic bonding via cation bridging. Maximum adsorption of organic constituents occurred at pH 6.3 on the  $\text{Fe}(\text{OH})_3$  treated soil with clover amendment compared to pH 6.2 for  $\text{Fe}(\text{OH})_3$  untreated soil. After 6 m of investigation, solid  $\text{Fe}(\text{OH})_3$  and soil  $\text{Fe}(\text{OH})_3$  remained in an amorphous state.

Fig. 3-10 Differential Scanning Calorimetry Plot of  
Orangeburg Topsoil With  $\text{Fe}(\text{OH})_3$  Addition.

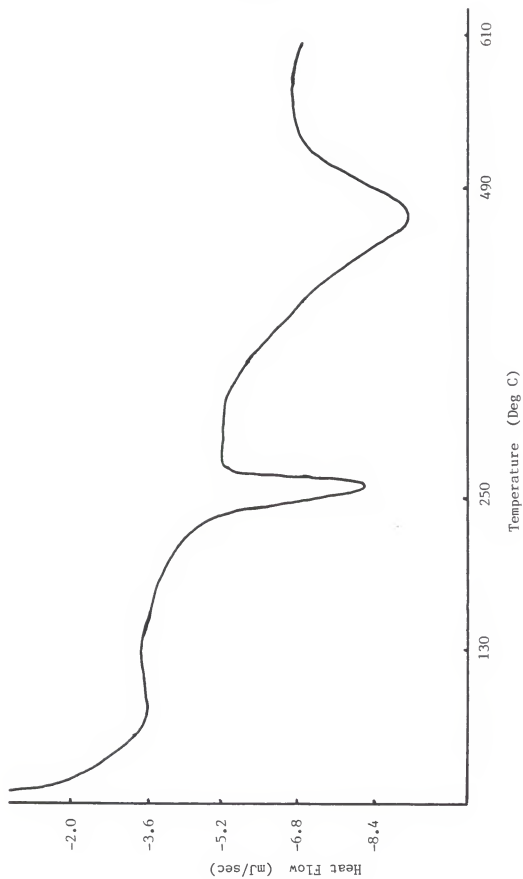
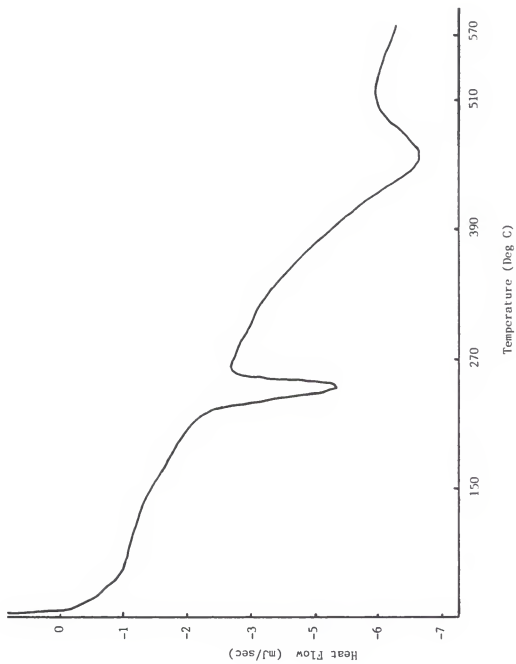




Fig. 3-11

Differential Scanning Calorimetry Plot of  
Orangeburg Topsoil with  $\text{Fe}(\text{OH})_3$  and Clover  
Addition.



## CHAPTER IV PHOSPHATE AND ORGANIC AMENDMENT STUDY

### Introduction

Reduction of plant available phosphorus in acidic soils causing an agronomic yield reduction has plagued man for many years. The problem is produced by reactions of phosphates with Fe and Al hydroxides, aluminosilicates and/or the ions released from dissolution of these minerals (Chu et al., 1962; Lindsay, 1979; Fox, 1974; Hingston et al., 1974).

A possible management alternative for reducing P sorption could be addition of organic amendments. Moshi et al., (1974) measured phosphate adsorption from two profiles (one cultivated and one under forest environment) of Kikuyu red clay from Kenya. They reported that surface-adsorbed organic components reduced the positive charge on mineral surfaces. There was a high statistical linear correlation between increasing percentage organic carbon and reducing positive charge. Since positive charge was reduced, phosphate adsorption at pH 5.0 was reduced by the presence of organic matter. Hinga (1973) obtained similar results on Kenya soils. Yuan (1980) found that pretreatment with organic material resulted in partial reduction of P fixation on a Paleudult.

Mechanisms producing reduction in P fixation might include 1) release of P for organic components, 2) blockage of P-adsorption sites with decompositional products from organic amendment, 3) complexation of solution Al and Fe by organic functional groups, and 4) solubilization of fertilizer reaction products such as dicalcium phosphate (DAP) by acidity produced from the humification process (Singh and Jones, 1976). The objectives of this study are to assess the effectiveness of clover addition to highly-weathered soils in reducing P fixation as measured by dry matter plant yield, P uptake, extractable P levels, and changes in surface charge on soil colloids.

### Materials

#### Soil

An Orangeburg topsoil as described in Chapter 3 was used in the clover amendment experiment. Amorphous  $\text{Fe}(\text{OH})_3$  was prepared and applied as described by previous methodology. The soil was limed to pH 6.3 utilizing the liming curve developed during preliminary experimentation, and incubated for 2 wk at 25°C at 10% moisture on a weight basis. Dried and ground clover was then completely mixed with predetermined treatments and incubated for 30 d prior to fertilizer addition.

### Clover

White clover was grown hydroponically to insure reactivity of organic functional groups. Hydroponic methodology is described in Chapter 3.

### Fertilizer

Pots used in the glasshouse study contained 3 kg of soil on a dry weight basis. Fertilizer applications (N, P, K, Mg) were adjusted by treatment assuming 50% mineralization from clover application. Total nutrient addition included 100 mg N/kg as  $\text{NH}_4\text{NO}_3$ , 140 mg K/kg as KCl. Diammonium phosphate was applied at rates equivalent to 0, 50, and 100 mg P/kg. Supplemental nutrient addition to pots included 19.8 mg Mg as  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ , 11.4 mg Zn as  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ , 5.09 mg Ca as  $\text{CaSO}_4 \cdot 5\text{H}_2\text{O}$  and 1.2 mg B as  $\text{Na}_2\text{B}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$ .

### Methods

#### Incubation Study

To investigate soil P retention, an incubation study was conducted with three soils. These were Orangeburg, Orangeburg + 5.6 g Fe/kg as  $\text{Fe}(\text{OH})_3$ , and Orangeburg subsoil. Each soil was amended with dried and ground clover at rates of 0, 1.58, and 3.16 g/kg over times of 30, 60, 90 d. Each soil had been previously limed to pH 6.3 and incubated for 2 w. Soil P retention was determined at each time interval by shaking 5 g of sieved soil with 100 ml of solution containing 100 mg P/L as  $\text{K}_2\text{PO}_4$  for 6 h (Fassbender and

Igue, 1967) in duplicate. After shaking, aliquots were filtered through a 0.2  $\mu$ m membrane filter disk and analyzed for orthophosphate (Murphy and Riley, 1962). Phosphorus fixation was determined by subtraction. Soil pH at each time interval was determined in a 1:1 soil to water suspension. Analysis of variance was performed on the split plot design utilizing time as a main plot with soil and clover addition as subplots.

#### Glasshouse Study

A 3 X 2 X 3 factorial experiment using 0, 50, and 100 mg P/kg soil, 0 and 5.6 g Fe/kg as  $\text{Fe}(\text{OH})_3$  and 0, 1.58 and 3.15 g clover/kg in split-split plot design with three replications was conducted in a glasshouse. Phosphate addition was the main plot with  $\text{Fe}(\text{OH})_3$  addition as the sub plot, and clover addition the sub-sub plot. Two crops of Zea mays L. were grown for 50 d each to determine initial and residual effectiveness of fertilizer. Treatments were limed and refertilized with previous rates before initiation of a third crop. Variables measured include dry matter yield, uptake of P, Ca, Mg and K, Al and Fe concentrations within plant tissue. Soil measurements included Truog and Bray 2 extractable P levels, soil pH, and organic C levels. Plant samples were analyzed in the following manner: 0.10 g of dried and ground tissue, passing a 1 mm sieve, was placed in a 50 mL beaker and oxidized in a muffle furnace at 450°C. The ash was further digested

with 3 M  $\text{HNO}_3$ , evaporated to dryness on a hotplate, with removal of excess  $\text{HNO}_3$  by placing each beaker into the muffle furnace at  $450^\circ\text{C}$  for 10 m. After cooling, 25 mL of 5 M  $\text{HCl}$  were added to the beaker, placed on a hotplate and evaporated to dryness to completely oxidize plant material. After cooling, 1 mL of 5 M  $\text{HCl}$  was placed in the beaker with water and diluted to a final volume of 50 mL. Ionic concentrations of Ca, Mg, K, Al, and Fe were determined by Inductively Coupled Argon Plasma spectrophotometry. Plant P concentrations were determined by methodology described by Murphy and Riley (1962).

Soils were sampled after each maize crop. Soil pH was determined in 1:1 soil to water ratio (McLean, 1982). Organic C levels were determined by methodology described by Walkley and Black (1934).

Since reaction products of DAP are  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ ,  $\text{CaHPO}_4$ , and colloidal ferric phosphate with Orangeburg soil, proper extractants needed to be chosen for extraction of these phases. Ballard (1974) compared various extractant effectiveness on a variety of phosphate reaction products as independent solid phases and those phases mixed with soil. In his research Truog reagent (0.001 M  $\text{H}_2\text{SO}_4$  + 3 g  $(\text{NH}_4)_2\text{SO}_4$ ) extracted 100% of P applied as dicalcium phosphate (DCP) as a solid phase and 98% DCP mixed with Leon fine sand. Only 2% of P applied as colloidal ferric phosphate (CFP) as a

solid and mixed with Leon fine sand was extracted. Bray 2 ( $0.03 \text{ M NH}_4\text{F} + 0.1 \text{ M HCl}$ ) extracted 98% P from CFP and CFP mixed with Leon fine sand. Sequential extractions for P were performed with Truog and Bray 2 solutions. Extraction methodology was as follows: 2 g of soil were placed in a centrifuge tube with 25 ml of Truog reagent. Samples were shaken at 180 excursions per minute for 30 m and centrifuged. Aliquots were filtered through Whatman #42 filter paper. Soil samples were again extracted with Bray 2 solution. Twenty mL of extractant were added to the soil sample and shaken for 1 m. Aliquots were immediately filtered through Whatman #42 filter paper. Soil P concentrations were determined by methodology described by Murphy and Riley (1962).

#### Surface Charge

To determine net electric charge and ZPC of 1)  $\text{Fe}(\text{OH})_3$  treated soil, 2)  $\text{Fe}(\text{OH})_3$  treated soil + 100 mg P/kg, 3)  $\text{Fe}(\text{OH})_3$  treated soil + 3.15 g clover/kg, and 4)  $\text{Fe}(\text{OH})_3$  treated soil + 100 mg P/kg + 3.15 g clover/kg, potentiometric titrations were performed. Samples were obtained after the first cropping period of the glasshouse experiment. Methodology described by Laverdiere and Weaver (1977) was performed in which 10 g of sample were weighed into 250 mL beakers with addition of 100 mL either 0.01, 0.1 or 1.0 M NaCl. Samples were allowed to equilibrate for 60 m and pH was



determined. Soil suspensions were titrated with 0.02 M HCl under continuous stirring. Salt solutions without soil were also titrated as a baseline for charge determination by subtracting  $H^+$  concentrations of blank titrations at a given pH from  $H^+$  concentrations of the soil suspension.

#### SEM Study

Clay fractions from 1) Orangeburg +  $Fe(OH)_3$  + P, and 2) Orangeburg +  $Fe(OH)_3$  + P + 3.15 g clover/kg for study under the scanning electron microscope were obtained by sieving the soil through a 300-mesh sieve, washing with water at pH 10, and collecting the aliquot. The clay-silt suspensions were centrifuged for 5 m at 1500 RPM. Gravimetric determinations of clay in suspension was performed. Samples were diluted by factors of 2, 3, 5 and 10, applied on a carbon-coated stub, and magnified within ranges of 450X to 10,000X.

### Results and Discussion

#### Incubation Study

An incubation study was developed to determine effects of time, soil, and clover amendment relating to P fixation capacity of the soil. As shown in Table 4-1, a triple order interaction was obtained. Phosphate fixation capacity was affected by times of 30, 60, or 90 d of incubation, clover application at rates of 0, 1.58 and 3.15 g/kg and the type of soil matrix.

Table 4-1. Effect of Experimental Parameters on  
P Retention Capacity

Source	df	Mean Square	p>F
Time	2	279999	0.0001
REP	1	2759	0.39
Error a	2	1245	
Soil	2	550367	0.0001
Clover	2	3058	0.44
Soil X Time	4	11426	0.03
Clover X Time	4	13726	0.02
Soil X Clover	4	11474	0.03
Soil X Clover			
X Time	8	13491	0.01
Error b	24	3611	

Since a triple order interaction was obtained, response surface equations were developed for each soil over clover application rates at each time of comparison. Equations are given in Table 4-2. Graphs of results at each time interval are given in Fig. 4-1 through 4-3.

#### Orangeburg Topsoil

Orangeburg topsoil is a sandy soil (85% sand, with iron concretions (0.31%)). Increasing rates of application of clover increased P fixation capacity after 30 d. After decomposition of clover, organic functional groups were available for reaction with soil components. Calcium can be bound ionically to organic functional groups (Bloom and McBride, 1979) thereby attaching orthophosphate to organic components and reducing P concentration in solution. With clover addition there was an increase in soil pH from 6.4 to 6.7. Differences in pH could also be induced by precipitation of DCP.

After 60 d of incubation, there was a slight increase in soil pH from 6.4 to 6.7 without clover treatment. Increased P fixation was also noted possibly due to the formation of a calcium phosphate precipitate. Clover-amended treatments decreased P fixation capacity, although it remained higher than the 0 clover application rate. Singh and Jones (1976) reported decreases in P fixation capacity of organic

Table 4-2. Response Surface Equations Relating P Fixation Capacity of Soils With Clover Addition Over Time.

Time (d)	Response Surface Equation	Correlation Coefficient
<u>Orangeburg</u>		
30	$P \text{ fix} = 196 - 81 \text{ clover} + 69 \text{ clover}^2$	$r^2 = 0.71$
60	$P \text{ fix} = 202 - 6 \text{ clover} + 8 \text{ clover}^2$	$r^2 = 0.49$
90	$P \text{ fix} = 274 + 252 \text{ clover} - 76 \text{ clover}^2$	$r^2 = 0.67$
<u>Orangeburg + 5.6 g Fe</u>		
30	$P \text{ fix} = 986 - 467 \text{ clover} + 111 \text{ clover}^2$	$r^2 = 0.83$
60	$P \text{ fix} = 240 + 107 \text{ clover} - 36 \text{ clover}^2$	$r^2 = 0.78$
90	$P \text{ fix} = 517 + 72 \text{ clover} - 21 \text{ clover}^2$	$r^2 = 0.29$
<u>Orangeburg Subsoil</u>		
30	$P \text{ fix} = 936 - 177 \text{ clover} + 41 \text{ clover}^2$	$r^2 = 0.30$
60	$P \text{ fix} = 684 - 130 \text{ clover} + 26 \text{ clover}^2$	$r^2 = 0.99$
90	$P \text{ fix} = 810 - 116 \text{ clover} + 33 \text{ clover}^2$	$r^2 = 0.83$

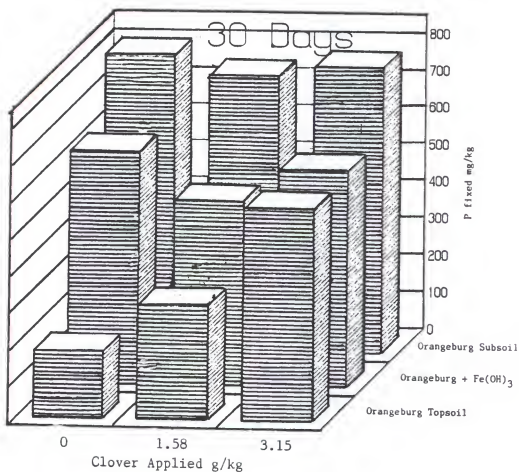


Fig. 4-1

Phosphate Fixation Capacity of Soils Amended With Various Clover Rates After 30 Days of Incubation.

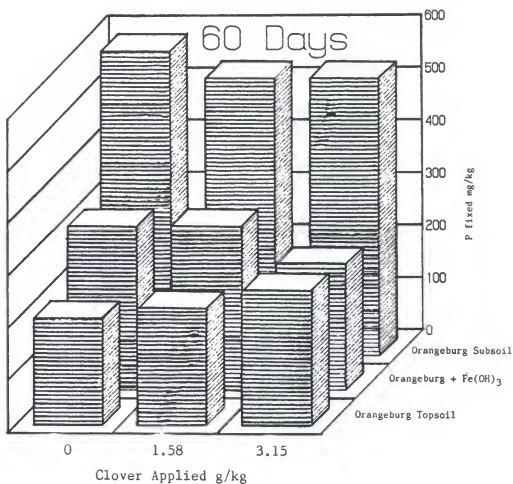


Fig. 4-2 Phosphate Fixation Capacity of Soils Amended With Various Clover Rates After 60 Days of Incubation.

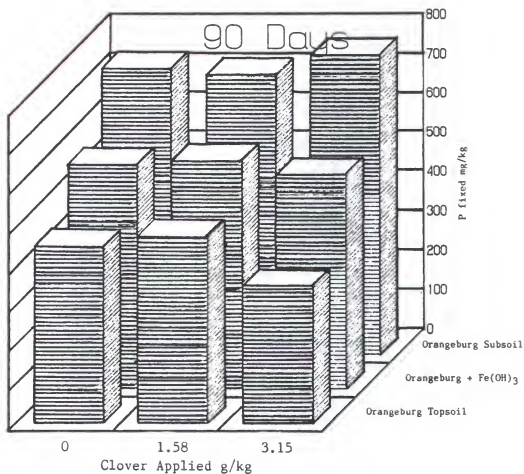


Fig. 4-3

Phosphate Fixation Capacity of soils  
Amended With Various Clover Rates After 90  
Days of Incubation.

treated soils after 30 d incubation due to P mineralization from organic substrates. Mineralization of P from microbial populations may have produced this result.

After 90 d of incubation, there was a slight decrease of soil pH from 6.6 to 6.3 without clover treatment. Increased P fixation was observed compared to 30 and 60 d incubation periods. The 3.15 g/kg clover treatment remained stable with respect to P fixation data from 60 d incubation time. However the 1.58 g/kg clover treatment increased soil P fixation capacity.

#### Orangeburg Topsoil + $\text{Fe}(\text{OH})_3$

After 30 d of incubation, treatments receiving clover applications possessed lower P fixation capacities than did treatments without clover application. Treatments receiving 1.58 g/kg clover had a lower P fixation capacity than 3.15 g clover/kg. Possibly decomposition products of clover were bound to the iron hydroxide surface as was the case in the clover amendment experiments of blocking positive charged sites available for P fixation. Soil pH ranged from 6.5 to 7.2 so that acid forming ions of Al, Fe, and Mn were not available for precipitation or ionically binding orthophosphate to organic components. Precipitation of calcium phosphates at pH 7.2 from the 3.15 g clover/kg



soil treatment may have occurred thereby increasing P fixation capacity for that treatment.

After 60 d of incubation, total P fixation of all treatments was reduced, possibly due to P mineralization from microbes and clover residues. Decreasing P fixation with increasing clover application was observed. Soil pH also increased possibly due to a self-limiting effect of  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$  with hydroxyl release from water applications reducing net positive charge and P-fixation capacity.

After 90 d of incubation, P fixation capacity was increased to near initial levels. Clover-amended treatments, although lower in P-fixation capacity than unamended treatments, did not produce substantial P-fixation reduction as was noted initially.

#### Orangeburg Subsoil

Orangeburg subsoil contains 34% material in the clay-size fraction with kaolinite as the dominant clay mineral. The clay surface is coated with goethite which is 1.3% of the total weight of the soil. Orangeburg subsoil results are similar to those obtained from Orangeburg +  $\text{Fe}(\text{OH})_3$  but clover application has less effect in reducing P fixation. Clover application at 30 d reduced P-fixation slightly compared to untreated soil. Greater total surface area of goethite with Orangeburg subsoil compared to  $\text{Fe}(\text{OH})_3$

applied to Orangeburg topsoil reduced clover-amendment effectiveness.

At 60 d of incubation, similar trends of reduction in P fixation capacity with increased soil pH were observed. Clover amendments lowered P fixation capacity compared to treatments without clover.

At 90 d, the effectiveness of the clover amendment was negligible.

#### Glasshouse Study

A glasshouse study was conducted to determine clover amendment effectiveness in reducing P fixation in relation to crop production. Three crops of maize were grown for 50 d each. Results from experimental parameters from each cropping period will be discussed.

##### Crop 1

##### Yield

Dry matter yield was affected by P rate,  $\text{Fe}(\text{OH})_3$  addition, and clover application as determined by a triple-order interaction. As seen in Table 4-3 and Fig. 4-4, without application of P, no difference in yield was obtained with clover applications on the  $\text{Fe}(\text{OH})_3$  treated soil. Ferric hydroxide provided a sink for indigenous soil P to be bound as well as P available from mineralization of clover. Without  $\text{Fe}(\text{OH})_3$  addition, yield was increased from clover applications with P additions. This effect could have been from clover functional groups binding

Table 4-3 Yield Response Surface Equations Obtained  
From the First Cropping Period.

Clover applied g/kg	Response Surface Equation	Correlation Coefficient
<u>P = 0 mg/kg</u>		
0	$Y = 0.97 - 0.07 \text{ Fe}$	$r^2 = 0.61$
1.58	$Y = 0.73 - 0.04 \text{ Fe}$	$r^2 = 0.18$
3.15	$Y = 3.17 - 0.48 \text{ Fe}$	$r^2 = 0.68$
<u>P = 50 mg/kg</u>		
0	$Y = 2.07 - 0.22 \text{ Fe}$	$r^2 = 0.73$
1.58	$Y = 2.13 - 0.20 \text{ Fe}$	$r^2 = 0.52$
3.15	$Y = 5.43 - 0.61 \text{ Fe}$	$r^2 = 0.63$
<u>P = 100 mg/kg</u>		
0	$Y = 6.57 - 0.88 \text{ Fe}$	$r^2 = 0.95$
1.58	$Y = 3.37 - 0.17 \text{ Fe}$	$r^2 = .18$
3.15	$Y = 5.37 - 0.20 \text{ Fe}$	$r^2 = 0.25$

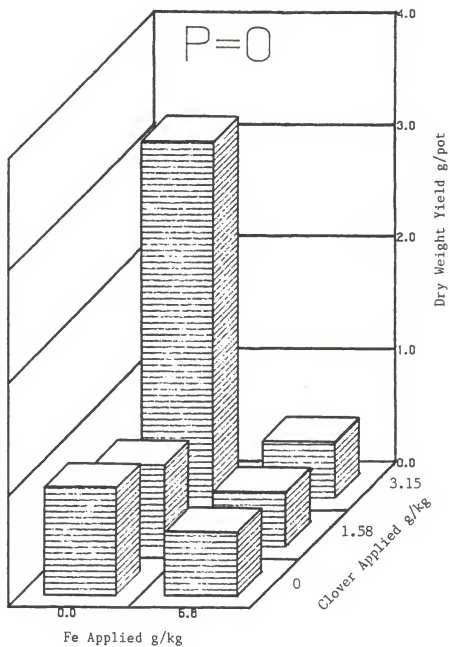


Fig. 4-4 Plant Dry Weight Yield Affected by  $\text{Fe}(\text{OH})_3$  and Clover Application at the 0 mg/kg  $\text{P}$  Rate During the First Cropping Period.

to Al or Fe ions from solution reducing precipitation of indigenous soil P. Although no differences in soil pH were observed, the pH of both soils had dropped to 5.2 which would increase Al and Fe activity in solution. Also, this effect may have been produced by P released from clover mineralization. Initially, P fertilizer was added (7.0 mg P/kg) to the clover control and 3.5 mg P/kg to the 1.58 g clover/kg treatment since the literature suggests that approximately 50% of organic P is released as orthophosphate (Lockett, 1938). Application of 3.58 g clover/kg was equivalent to adding 14 mg P/kg soil. Possibly release of P from clover later in the cropping period resulted in enhanced yield rather than immediate solubilization of fertilizer P.

Application of 50 mg P/kg increased plant yield compared to that without P.  $\text{Fe}(\text{OH})_3$  again decreased plant yield. However, increasing application rates of clover increased plant yield on  $\text{Fe}(\text{OH})_3$  treated soil (Table 4-3 and Fig. 4-5). It appeared that P was more available on  $\text{Fe}(\text{OH})_3$  treated soils due to blockage of P adsorption sites by organic ligands from clover application. Increase in yield of treatments without  $\text{Fe}(\text{OH})_3$  addition may have been produced by binding Al and Fe by organic ligands. Doubling of dry matter yield from clover addition of 3.18 g

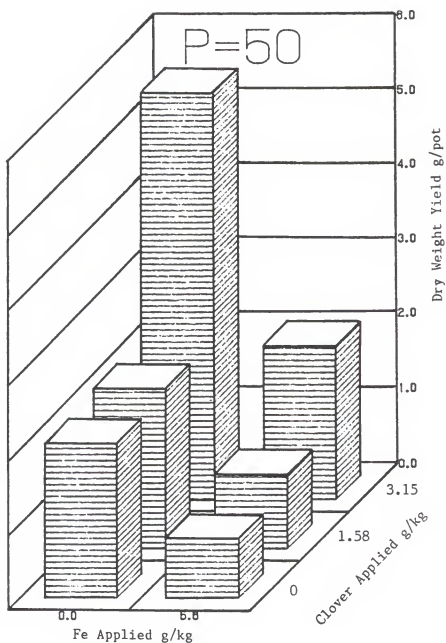


Fig. 4-5 Plant Dry Weight Yield Affected by  $\text{Fe}(\text{OH})_3$  and Clover Applications at the 50 mg/kg P Rate During the First Cropping Period.

clover/kg soil could not have been produced solely by P release at the rate of 7.0 mg P/kg) .

Applications of 100 mg P/kg increased dry weight yield compared to the 50 mg P/kg rate (Table 4-3 and Fig. 4-6). Ferric hydroxide treatments decreased maize yield but an incremental increase in yield was observed with increasing clover applications. Yield was more than tripled when clover was applied at 3.15 g clover/kg soil. Phosphorus availability appeared to be greater due to clover pretreatment. Results agree with the previous incubation study relating to P availability with  $\text{Fe}(\text{OH})_3$  treatment in acidic (pH 5.2) ranges. Greater yield was obtained without clover application if  $\text{Fe}(\text{OH})_3$  was not introduced into the soil system. Cation bridging of P to organic functional groups may have produced this result.

#### P uptake

Phosphorus uptake by maize plants was affected by amount of P or  $\text{Fe}(\text{OH})_3$  applied. Increasing P rates increased P in plants while addition of  $\text{Fe}(\text{OH})_3$  reduced P uptake. With increasing rates of clover applied (Table 4-4 and Fig. 4-7, 4-8 and 4-9), enhanced P uptake was obtained. Mechanisms relating to clover amendment effectiveness were not determined. Yield data appears to relate well to P uptake observations. Binding of Fe or Al by organic functional groups or

Table 4-4 Phosphorus Uptake Response Surface Equations Obtained From First Cropping Period.

Clover applied g/kg	Response Surface Equation	Correlation Coefficient
0	P uptake = .004 + 0.06 P + 0.05 Fe - 0.01 P*Fe	$r^2 = .91$
1.58	P uptake = .37 + .04 P - .02 Fe - .003 P*Fe	$r^2 = .74$
3.15	P uptake = 1.90 + .05 P - .26 Fe - .004 P*Fe	$r^2 = .72$



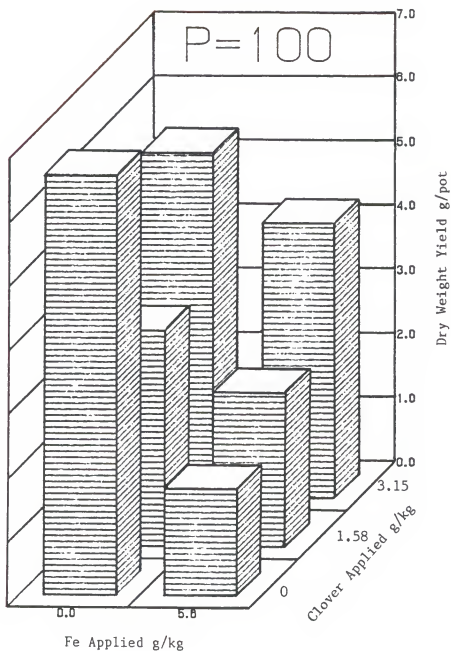


Fig. 4-6 Plant Dry Weight Yield Affected by  $\text{Fe}(\text{OH})_3$  and Clover Applications at the 100 mg/kg P Rate During the First Cropping Period.

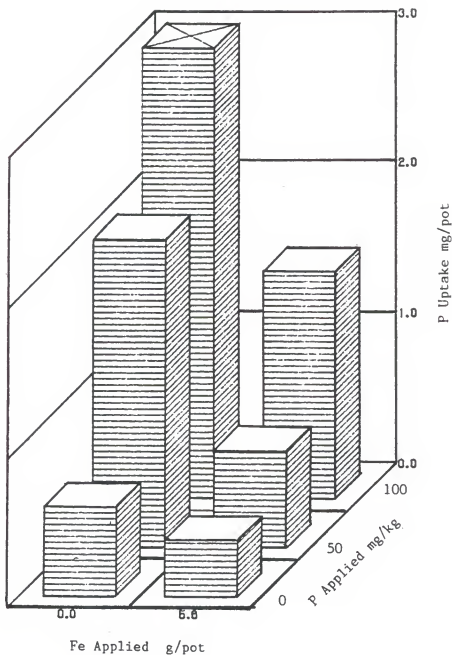


Fig. 4-7 Phosphorus Uptake by Maize as Affected by  $\text{Fe}(\text{OH})_3$  and P Application at the 0 g/kg Clover Rate During the First Cropping Period.

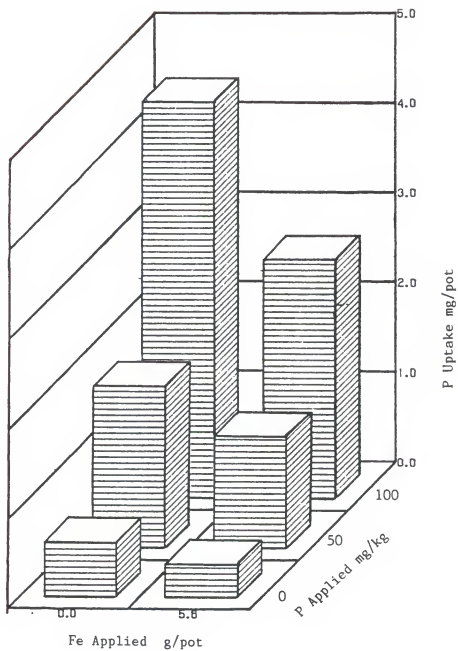


Fig. 4-8 Phosphorus Uptake by Maize as Affected by  $\text{Fe}(\text{OH})_3$  and P Application at the 1.58 g/kg Clover Rate During the First Cropping Period.

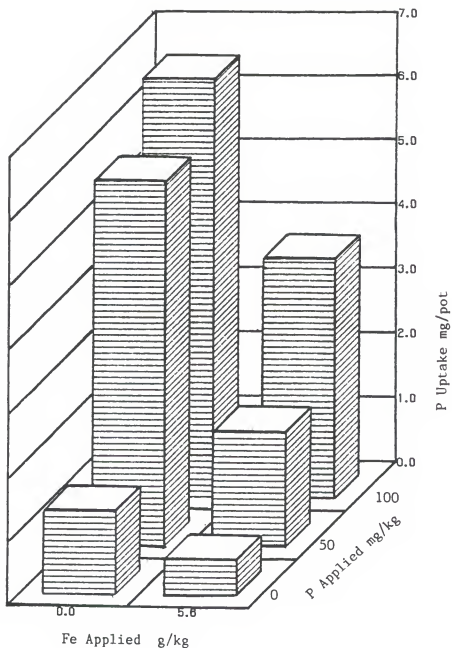


Fig. 4-9 Phosphorus Uptake by Maize as Affected by  $\text{Fe}(\text{OH})_3$  and P application at the 3.15 g/kg Clover Rate During the First Cropping Period.

bonding of organic ligands to  $\text{Fe}(\text{OH})_3$  surfaces would explain the results obtained.

#### Truog Extractable P

A reaction product of DAP is dicalcium phosphate (Lindsay, 1959). Truog reagent is a good extractant for this phase (Ballard, 1974). Preliminary extraction with Truog reagent produced an Fe-clover interaction. Addition of  $\text{Fe}(\text{OH})_3$  reduced Truog extractable P levels drastically (Fig. 4-10, 4-11 and 4-12). Without clover application, P addition of 100 mg/kg slightly increased Truog P levels which would apply to the dicalcium phosphate fraction. Inconclusive results were obtained with  $\text{Fe}(\text{OH})_3$  treated soils regardless of rate of P application. Without  $\text{Fe}(\text{OH})_3$  application, increases in Truog extractable P resulted from clover application at increasing P rates (Table 4-5). Previous mechanisms, discussed above appeared to have produced these effects.

#### Bray 2 Extractable P

Orthophosphate adsorption to iron mineral surfaces reduces plant available P. Bray 2 extraction is a good method for determining slightly soluble or desorbable P reaction products. Bray 2 extractable P was affected by main effects of P rate,  $\text{Fe}(\text{OH})_3$  amendment, and

Table 4-5 Truog Extractable P Levels Determined After the First Cropping Period.

Response Surface Equation		Correlation Coefficient
<u>P Applied (0 mg/kg)</u>		
Truog P = 3.05 - 0.43 Fe + 0.30 clover - 0.05 Fe clover		$r^2 = 0.40$
<u>P Applied (50 mg/kg)</u>		
Truog P = 5.43 - 1.00 Fe + 0.46 clover - 0.05 Fe clover		$r^2 = 0.95$
<u>P Applied (100 mg/kg)</u>		
Truog P = 7.02 - 0.99 Fe + 1.07 clover - 0.21 Fe clover		$r^2 = 0.78$

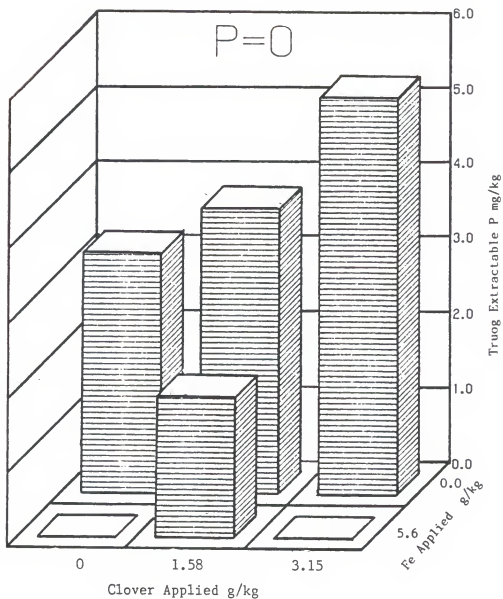


Fig. 4-10 Truog Extractable P Levels as Affected by Clover and  $\text{Fe}(\text{OH})_3$  Applications at the 0 mg/kg P Rate During the First Cropping Period.

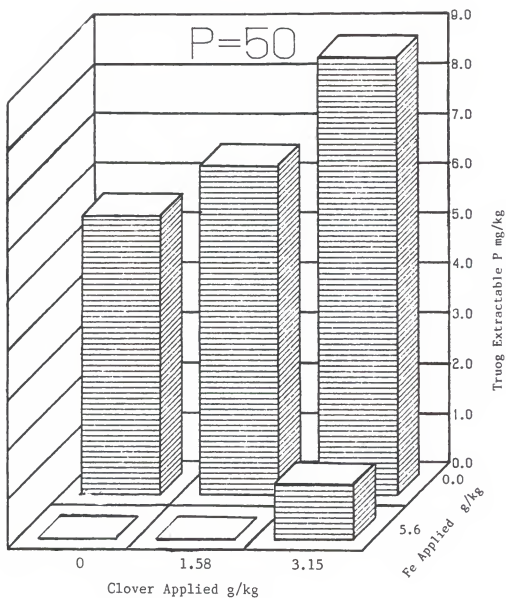


Fig. 4-11 Truog Extractable P Levels as Affected by Clover and  $\text{Fe}(\text{OH})_3$  Applications at the 50 mg/kg P Rate During the First Cropping Period.



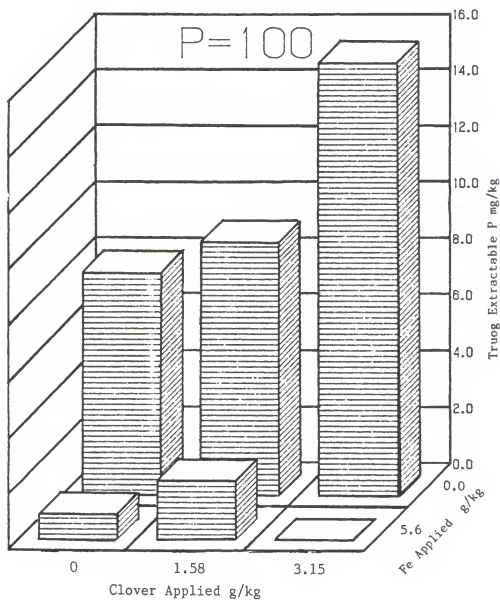


Fig. 4-12 Truog Extractable P Levels as Affected by Clover and  $\text{Fe}(\text{OH})_3$  Applications at the 100 mg/kg P Rate During the First Cropping Period.

clover application, as shown in Table 4-6. With increasing P rates, significant increases were observed in Bray 2 extractable P levels probably from adsorption to the iron mineral surface. Binuclear adsorption would reduce extractable P results due to the stability of the adsorption bond and the irreversible nature of the adsorption. Clover amendments increased extractable P availability. Possible mechanisms of organic ligand adsorption, Al and Fe complexation, P release for clover and/or acid humification processes solubilizing calcium phosphates, could increase extractable P concentrations.

#### Organic Carbon

No significance with respect to organic carbon levels was found with clover pretreatment. Further monitoring of this experimental parameter was terminated.

#### Crop 2

A second maize crop, grown for 50 d, was initiated to determine residual treatment effectiveness in relation to experimental parameters.

#### Yield

Plant dry weight yield was influenced by previous  $\text{Fe(OH)}_3$  and clover applications (Table 4-7). Main plot effects did not show increase in yield from previous

Table 4-6 Main Effects of P,  $\text{Fe}(\text{OH})_3$  and Clover Affecting Bray 2 Extractable P Levels From the First Cropping Period.

the first cropping period.			
P Applied (mg/kg)	Bray 2 Extractable P	Contrast	p>F
0	9.86		
50	20.01	0 vs others	0.01
100	27.84	50 vs 100	0.01
<hr/> Fe Applied (g/kg)			
0	26.06		
5.6	12.41	0 vs 5.6	0.05
<hr/> Clover Applied (g/kg)			
0	14.56		
1.58	18.13	0 vs others	0.01
3.15	25.02	1.58 vs 3.15	0.01

DAP application due to fixation mechanisms. Ferric-hydroxide decreased dry weight yield fourfold. Clover addition increased yield with each increasing rate of application. Since P was a limiting factor, clover applications apparently increased P reaction product availability. Release of P from clover should have subsided long before termination of the second cropping period. Yield was not likely to be reduced from Al or Fe toxicity at pH values of the soil. Although differences in Al and Fe levels within plant tissue existed (Table 4-8) with respect to  $\text{Fe}(\text{OH})_3$  treatment, Al and Fe levels were not at toxic concentrations.

#### P Uptake

Phosphorus uptake by maize was affected by  $\text{Fe}(\text{OH})_3$  addition (Table 4-9). The  $\text{Fe}(\text{OH})_3$  provided a sink for P adsorption. Also as seen in Table 4-10, soil pH had dropped to 5.0 such that  $\text{Al}^{3+}$  and  $\text{Fe}^{3+}$  could be in solution reducing P availability from precipitation reactions. Aluminum and Fe ions were present in soil solution as determined by plant uptake of these ions. Addition of  $\text{Fe}(\text{OH})_3$  resulted in a fourfold decrease in P uptake.

#### Truog Extractable P

Truog extractable P was affected by an interaction of  $\text{Fe}(\text{OH})_3$  and clover. Increasing levels of clover

Table 4-7 Main Effects of  $\text{Fe}(\text{OH})_3$  and Clover Treatments on Plant Yield During the Second Cropping Period.

Clopping period:			
Fe applied (g/kg)	Yield (g/pot)	Contrast	p>F
0	2.17	0 vs. 5.6	0.01
5.6	0.53		
Clover applied (g/kg)			
0	0.85	0 vs. others	0.01
1.58	1.35		
3.15	1.85	1.58 vs 3.15	0.01

Table 4-8 Main Effect of  $\text{Fe}(\text{OH})_3$  Addition on Al and Fe Concentrations in Plant Tissue After the Second Cropping Period.

	Al	Fe	Contrast	p>F
	----- mg/kg-----			
Plus $\text{Fe}(\text{OH})_3$	131	133	Plus vs Minus	0.01
Minus $\text{Fe}(\text{OH})_3$	83	83		

Table 4-9 Main Effect of  $\text{Fe}(\text{OH})_3$  Treatment on Plant P Uptake During the Second Cropping Period.

Fe (g/kg)	P uptake mean mg P/Pot	Contrast	p>F
0	2.15	0 vs 5.6	0.01
5.6	0.57		

Table 4-10 Main Effect of  $\text{Fe}(\text{OH})_3$  Treatment on Soil pH After Two Cropping Periods.

Fe (g/kg)	pH mean	Contrast	p>F
0	5.12	0 vs 5.6	0.01
5.6	4.95		

increased Truog P, as  $\text{Fe}(\text{OH})_3$  produced a reduction in P at each P application rate (Table 4-11). As the pH of the soil decreased, solubilization of indigenous soil P, or P from fertilizer reaction products increased producing measurable levels of Truog extractable P which is a P form readily available to plants. Without  $\text{Fe}(\text{OH})_3$  addition, increasing levels of Truog P were obtained with increasing clover rates, without added P. This same observation (Fig. 4-13) was also noted during the first cropping period. Reduction in Truog extractable P on  $\text{Fe}(\text{OH})_3$  treated soil without P addition with increasing clover rates may be explained by P utilized for plant growth. Increased maize yields were obtained with increasing clover application rates, which would lower Truog P levels. Similar observations were obtained at the 50 mg P/kg rate (Fig. 4-14) and the 100 mg P/kg rate (Fig. 4-15) with the exception that Truog extractable P levels also increased with increasing rate of P application.

#### Bray 2 Extractable P

Bray 2 extractable P levels were affected by interaction of P and  $\text{Fe}(\text{OH})_3$ . Extractable P was increased with increasing P rates but decreased with  $\text{Fe}(\text{OH})_3$  additions. Extractable P levels were increased

Table 4-11 Response Surface Equations of Truog Extractable P Levels After the Second Cropping Period.

Response Surface Equation	Correlation Coefficient
$\text{Truog P} = 2.48 + .05 \text{ Fe} + .28 \text{ clover} - .06 \text{ Fe clover}$	$r^2 = .36$
$\text{Truog P} = 5.06 - .45 \text{ Fe} + .41 \text{ clover} - .08 \text{ Fe clover}$	$r^2 = .96$
$\text{Truog P} = 7.75 - 0.92 \text{ Fe} + 0.61 \text{ clover} - 0.09 \text{ Fe clover}$	$r^2 = .96$



with increasing clover rates (Table 4-12 and Fig. 4-16, 4-17, and 4-18). Increases of Bray 2 extractable P from  $\text{Fe}(\text{OH})_3$  untreated soil compared to that for Crop 1 may have been produced by precipitation of Fe or Al phosphates with decreasing soil pH. Reversion of a calcium phosphate to a Fe or Al phosphate possessing greater stability would increase Bray 2 levels. Change in Bray 2 extractable P may be due to blockage of P fixation sites by organic ligands reducing the irreversible binuclear P adsorption.

### Crop 3

A third crop was grown for 50 d to determine clover effectiveness over time in increasing dry weight yield, P uptake, and Truog and Bray 2 extractable P. Each treatment was again limed to pH 6.3 utilizing the liming curve described in Chapter 3. Constant fertilizer amounts were applied. Rates of 0, 50, and 100 mg P/kg as DAP were applied to appropriate treatments.

### Yield

Dry matter yield was influenced by interaction of P with  $\text{Fe}(\text{OH})_3$  applications. (Table 4-13). Increasing rates of P increased dry weight yield (Fig. 4-19, 4-20 and 4-21). Observations of increases in yield on  $\text{Fe}(\text{OH})_3$  treated soil with increasing clover applications suggested that organic functional groups were bonded to Fe mineral surfaces, thereby reducing P

Table 4-12 Response Surface Equations of Bray 2  
Extractable P Levels After the Second  
Cropping Period.

Response Surface Equation	Correlation Coefficient
<u>Clover Applied (0 g/kg)</u>	
Bray P = 9.28 + .28 P - .85 Fe - .04 P Fe	$r^2 = .96$
<u>Clover Applied (1.58 g/kg)</u>	
Bray P = 16.99 + .24 P - 2.13 Fe - .02 P Fe	$r^2 = .97$
<u>Clover Applied (3.15 g/kg)</u>	
Bray P = 23.19 + .22 P - 2.62 Fe - .02 P Fe	$r^2 = .96$

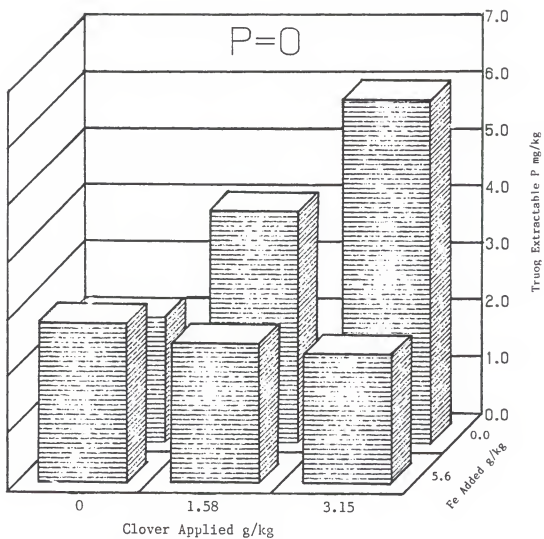


Fig. 4-13 Truog Extractable P Levels as Affected by Clover and  $\text{Fe}(\text{OH})_3$  Applications at the 0 mg/kg P Rate During the Second Cropping

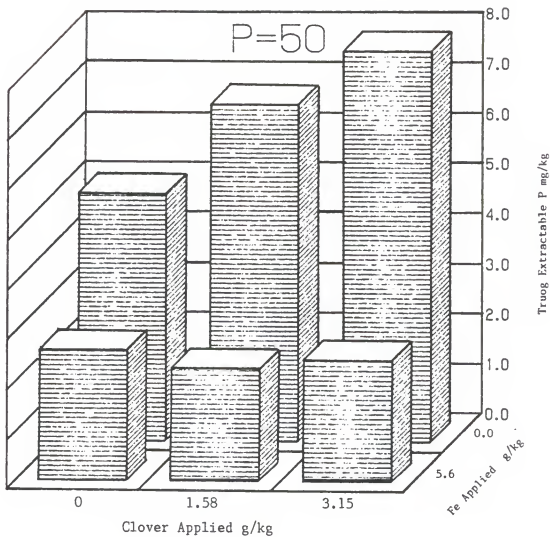


Fig. 4-14 Truog Extractable P Levels as Affected by Clover and  $\text{Fe}(\text{OH})_3$  Applications at the 50 mg/kg P Rate During the Second Cropping Period.

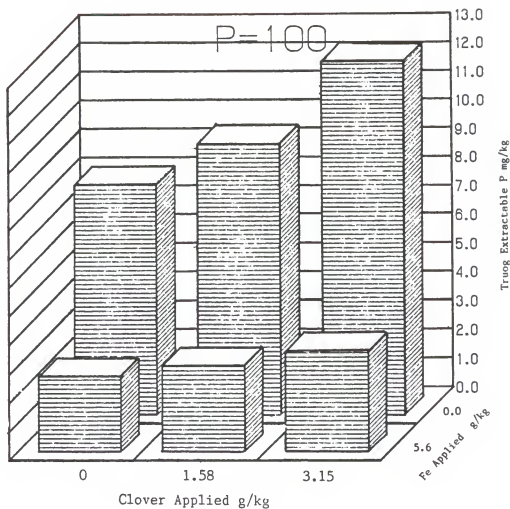


Fig. 4-15 Truog Extractable P Levels as Affected by Clover and  $\text{Fe}(\text{OH})_3$  Applications at the 100 mg/kg P Rate During the Second Cropping Period.

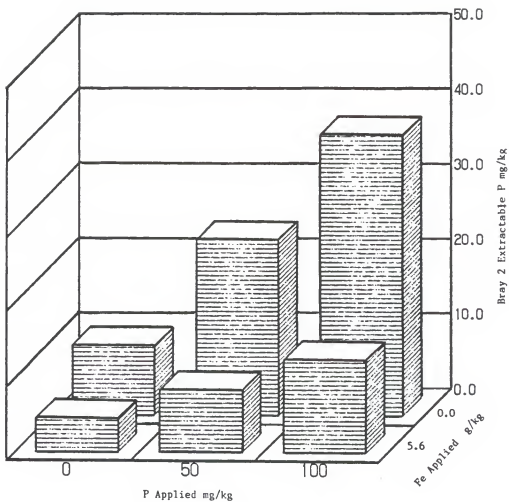


Fig. 4-16 Bray 2 Extractable P Levels as Affected by P and  $\text{Fe}(\text{OH})_3$  Applications at the 0 g/kg Clover Rate During the Second Cropping Period.

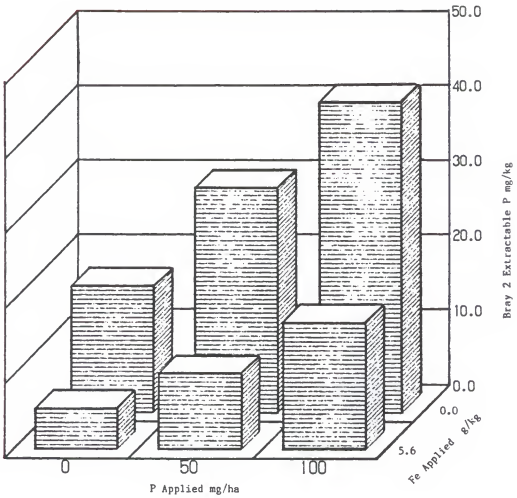


Fig. 4-17 Bray 2 Extractable P Levels as Affected by P and  $\text{Fe}(\text{OH})_3$  Applications at the 1.58 g/kg Clover Rate During the Second Cropping Period.

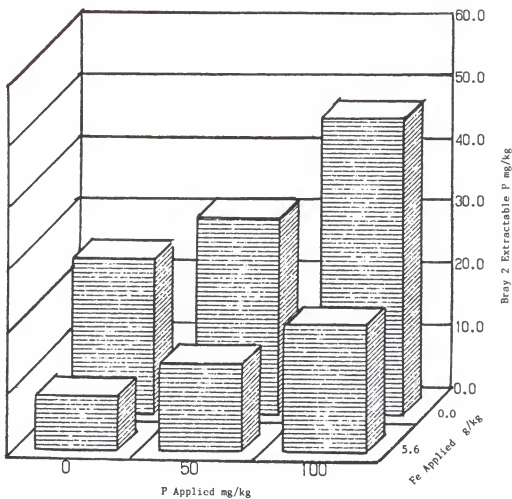


Fig. 4-18 Bray 2 Extractable P Levels as Affected by P and  $\text{Fe}(\text{OH})_3$  Applications at the 3.15 g/kg Clover Rate During the Second Cropping Period.



Table 4-13 Response Surface Equations of P and  $\text{Fe}(\text{OH})_3$  Across Clover Application Rates in Relation to Dry Weight Yield After the Third Cropping.

Response Surface Equation		Correlation Coefficient
<u>Clover Applied (0 g/kg)</u>		
Yield	$= .33 + .09 P + .12 \text{ Fe} - .01 P * \text{Fe}$	$r^2 = .76$
<u>Clover Applied (1.58 g/kg)</u>		
Yield	$= .88 + .06 P + .04 \text{ Fe} - .01 P * \text{Fe}$	$r^2 = .52$
<u>Clover Applied (3.15 g/kg)</u>		
Yield	$= 2.28 + .05 P - .23 \text{ Fe} - .002 P * \text{Fe}$	$r^2 = .53$

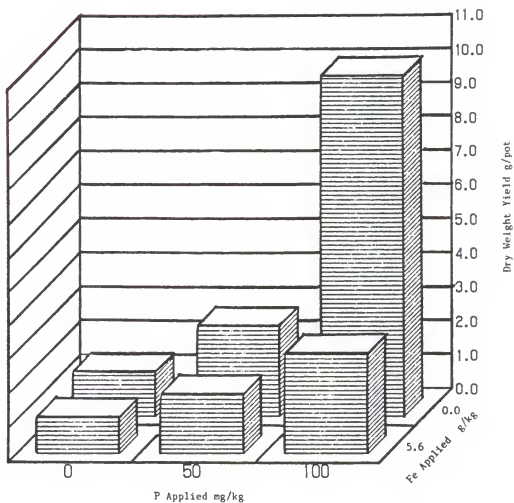


Fig. 4-19 Plant Dry Weight Yield as Affected by P and  $\text{Fe}(\text{OH})_3$  Applications at the 0 g/kg Clover Rate During the Third Cropping Period.

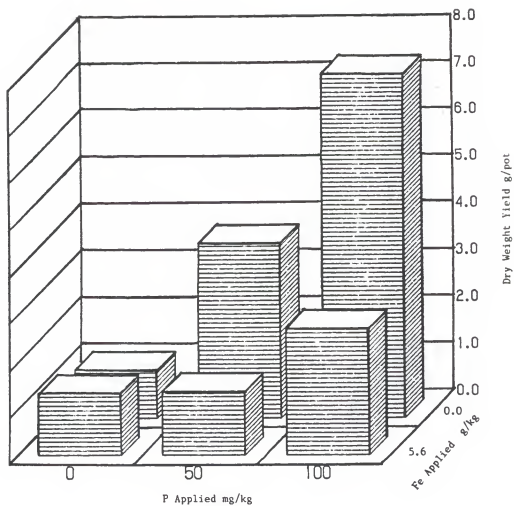


Fig. 4-20 Plant Dry Weight Yield as Affected by P and  $\text{Fe}(\text{OH})_3$  Applications at the 1.58 g/kg Clover Rate During the Third Cropping Period.

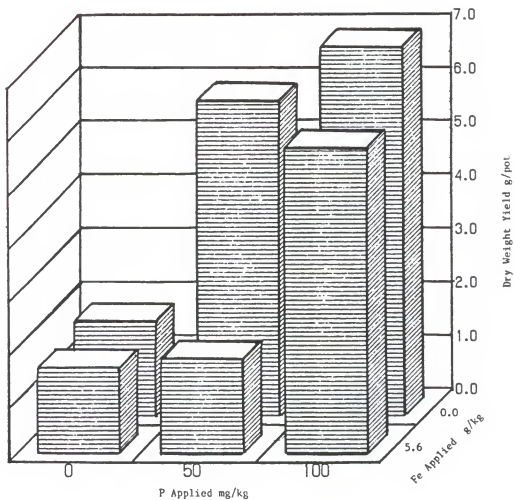


Fig. 4-21 Plant Dry Weight Yield as Affected by P and  $\text{Fe}(\text{OH})_3$  Applications at the 3.15 g/kg Clover Rate During the Third Cropping Period.

adsorption sites. At the 100 mg P/kg rate, addition of 3.15 g clover/kg increased yield 600% compared to treatments without clover addition. This effect was produced after an initial clover application and two previous cropping periods on the same soil. Stability exists in the effect produced by clover application on  $\text{Fe}(\text{OH})_3$  treated soil, whatever the mechanism. Without  $\text{Fe}(\text{OH})_3$  application, mixed results were obtained with P and clover application. At 50 mg P/kg, yield was increased with increasing clover addition but at 100 mg P/kg, yield was decreased with increasing clover rate of application.

#### P Uptake

A second application of fertilizer P masked the clover effect with respect to P uptake. As seen in Table 4-14, P uptake was affected by main effects of P and  $\text{Fe}(\text{OH})_3$  application. Increased rates of P application increased P uptake whereas addition of  $\text{Fe}(\text{OH})_3$  decreased P uptake.

#### Soil pH

Since the soil was limed before the third cropping period, reversion of soil pH to its natural state had not fully occurred. Differences in soil pH had developed with respect to  $\text{Fe}(\text{OH})_3$  addition (Table 4-15), but pH had not decreased to a state that would promote further extensive P fixation from Al or Fe

Table 4-14 Main Effects of P and  $\text{Fe}(\text{OH})_3$  Relating to  
Plant P Uptake From the Third Cropping.

	P uptake mg/pot	Contrast	p>F
<u>P Applied (mg/kg)</u>			
0	1.27	0 vs others	0.01
50	3.42	50 vs 100	0.01
100	8.01		
<u>Fe Applied (g/kg)</u>			
0	6.14	0 vs 5.6	0.01
5.6	2.33		

release into the soil solution or as sites for P retention.

#### Truog Extractable P

Truog extractable P levels were affected by an interaction of  $\text{Fe}(\text{OH})_3$  with clover (Table 4-16). Without  $\text{Fe}(\text{OH})_3$  addition, Truog extractable P levels increased with increasing P rates and clover additions. (Fig. 4-22, 4-23 and 4-24). With  $\text{Fe}(\text{OH})_3$  addition, Truog P levels were increased with clover application compared to without clover application. The  $\text{Fe}(\text{OH})_3$  addition reduced Truog P levels at each P and clover rate. Variability in Truog P levels on  $\text{Fe}(\text{OH})_3$  treated soils may result from differences in P taken up by plants causing reduction extractable P levels.

#### Bray 2 Extractable P

Bray 2 extractable P levels were affected by P rates,  $\text{Fe}(\text{OH})_3$  addition, and clover application rates as a triple-order interaction (Table 4-17). Increases in extractable P were linear with increasing clover applications (Fig. 4-25, 4-26, and 4-27) and also with increasing P rates. The  $\text{Fe}(\text{OH})_3$  applications reduced extractable P levels significantly. Although increases in extractable P were obtained with clover application on  $\text{Fe}(\text{OH})_3$  treated soil, increases were not as great

Table 4-15 Main Effect of  $\text{Fe}(\text{OH})_3$  Relating to Soil pH Changes During the Third Cropping Period.

Fe Applied (g/kg)	pH	Contrast	p>F
0	6.20		
5.6	5.28	0 vs 5.6	0.01

Table 4-16 Response Surface Equations of  $\text{Fe}(\text{OH})_3$  and Clover Across P Application Rates in Relation to Truog Extractable P Levels After the Third Cropping Period.

Response Surface Equation	Correlation Coefficient
<u>P Applied (0 mg/kg)</u>	
Truog P = 3.48 - .12 Fe + .20 clover - .03 Fe clover	$r^2 = .59$
<u>P Applied (50 mg/kg)</u>	
Truog P = 7.75 - .28 Fe + .57 clover - .10 Fe clover	$r^2 = .36$
<u>P Applied (100 mg/kg)</u>	
Truog P = 14.54 - 1.87 Fe + .77 clover - .10 Fe clover	$r^2 = .98$



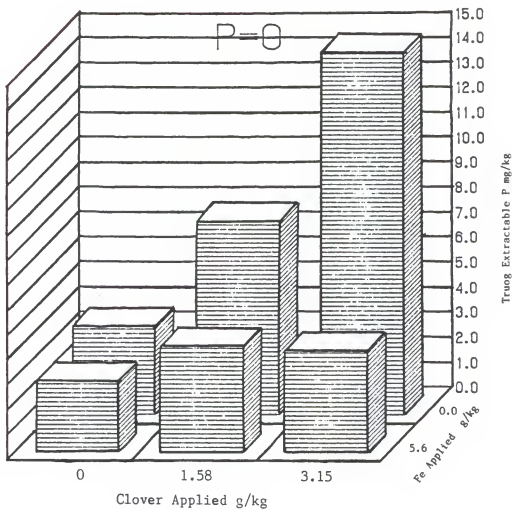


Fig. 4-22 Truog Extractable P Levels as Affected by Clover and  $\text{Fe}(\text{OH})_3$  Applications at the 0 mg/kg P Rate During the Third Cropping Period.

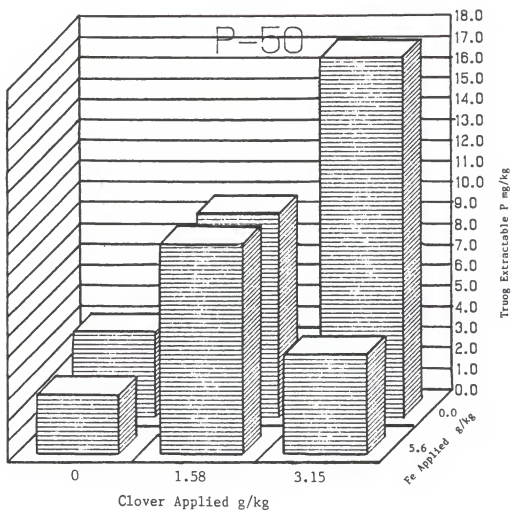


Fig. 4-23 Truog Extractable P Levels as Affected by Clover and  $\text{Fe}(\text{OH})_3$  Applications at the 50 mg/kg P Rate During the Third Cropping Period.

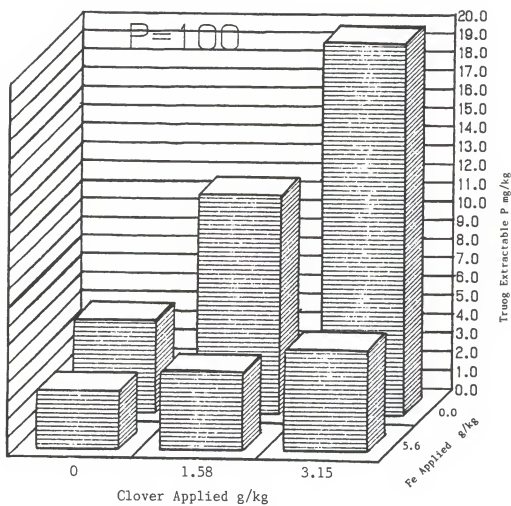


Fig. 4-24 Truog Extractable P Levels as Affected by Clover and  $\text{Fe}(\text{OH})_3$  Applications at the 100 mg/kg P Rate During the Third Cropping Period.

Table 4-17 Regression Equations of  $\text{Fe}(\text{OH})_3$  and Clover Application in relation to of Bray 2 Extractable P Levels After the Third Cropping.

Clover added (g/kg)	Regression Equations	Correlation Coefficient
<u>P Applied (0 mg/kg)</u>		
0	Bray P = 8.92 - .84 Fe	$r^2 = .95$
1.58	Bray P = 13.42 - .90 Fe	$r^2 = .41$
3.15	Bray P = 20.52 - 2.21 Fe	$r^2 = .95$
<u>P Applied (50 mg/kg)</u>		
0	Bray P = 32.92 - 3.76 Fe	$r^2 = .97$
1.58	Bray P = 39.60 - 4.73 Fe	$r^2 = .98$
3.15	Bray P = 42.53 - 3.73 Fe	$r^2 = .96$
<u>P Applied (100 mg/kg)</u>		
0	Bray P = 59.8 - 6.07 Fe	$r^2 = .96$
1.58	Bray P = 66.91 - 6.29 Fe	$r^2 = .99$
3.15	Bray P = 69.87 - 5.89 Fe	$r^2 = .98$

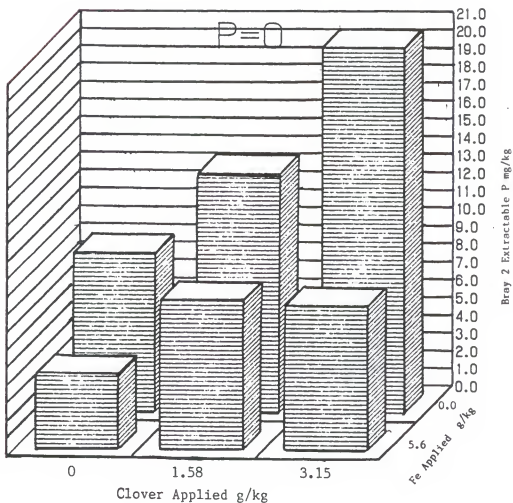


Fig. 4-25 Bray 2 Extractable P Levels as Affected by Clover and  $\text{Fe}(\text{OH})_3$  Applications at the 0 mg/kg P Rate During the Third Cropping Period.

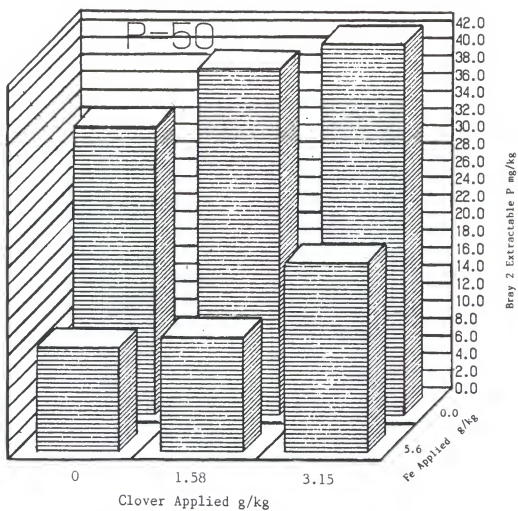


Fig. 4-26 Bray 2 Extractable P Levels as Affected by Clover and  $\text{Fe}(\text{OH})_3$  Applications at the 50 mg/kg P Rate During the Third Cropping Period.

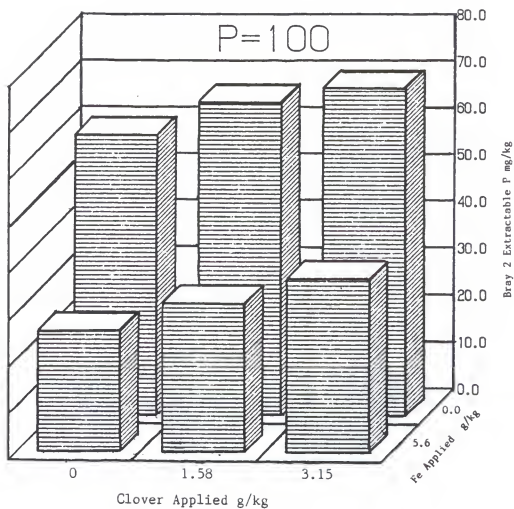


Fig. 4-27 Bray 2 Extractable P Levels as Affected by Clover and  $\text{Fe}(\text{OH})_3$  Applications at the 100 mg/kg P Rate During the Third Cropping Period.

with clover application as measured during other cropping periods with previous P application before cropping.

#### Surface Charge Study

Since differences in yield, P uptake, Truog extractable P and Bray 2 extractable P existed on  $\text{Fe}(\text{OH})_3$  treated soils with respect to P and clover addition, potentiometric titrations relating to variations in net electric surface charge and ZPC were determined. Addition of  $\text{Fe}(\text{OH})_3$  to kaolinite, the main clay component of Orangeburg soil, creates greater positive surface charge with reduced cation exchange capacity (Dixon, 1977). Experimental objectives included qualification and quantification of surface charge properties of Orangeburg soil samples treated with  $\text{Fe}(\text{OH})_3$  with applications of P, clover, and P and clover, from the glasshouse study.

#### Orangeburg + $\text{Fe}(\text{OH})_3$

Zero points of titration occur at pH values of 5.2 to 5.4 (Fig. 4-28) to  $\text{Fe}(\text{OH})_3$  treated Orangeburg topsoil. Since this treatment had been used in the glasshouse experiment, reversion of soil pH from 6.3 to 5.4 had occurred. A ZPC value was obtained at pH 4.0. Kaolinite, the major clay mineral in the Orangeburg soil, possesses ZPC values near this pH. Surface charge of 1.0  $\text{cmol}(+)/\text{kg}$  soil is probably produced by



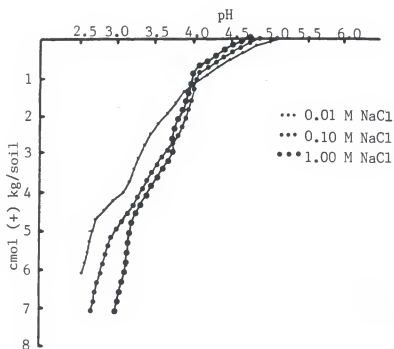


Fig. 4-28 Surface Properties of Orangeburg Topsoil +  $\text{Fe}(\text{OH})_3$  as Determined by Potentiometric Titration

$\text{Fe}(\text{OH})_3$  addition which increases net positive charge. However, the integrity of the kaolinite surface should not have been totally lost after addition of 5.6 g  $\text{Fe/kg}$  as  $\text{Fe}(\text{OH})_3$ .

Orangeburg +  $\text{Fe}(\text{OH})_3$  + P

Orthophosphate binds covalently to  $\text{Fe}(\text{OH})_3$  mineral surfaces releasing  $\text{OH}_2^0$  and  $\text{OH}^-$  ligands and produces a surface with greater net negative charge (Hingston et al., 1974). This reaction lowers the pH of the ZPC (Schwertmann and Taylor, 1977). From the results shown in Fig. 4-29, a decrease in ZPC pH from 4.0 to 3.5 had occurred suggesting covalent bonding of P to the iron mineral surface. Increase in positive charge (2  $\text{cmol}(+)/\text{kg}$  soil) indicates that  $\text{H}^+$  adsorption possibly occurs on a more negatively charged surface produced by orthophosphate specific adsorption with lowering of kaolinite ZPC.

Orangeburg +  $\text{Fe}(\text{OH})_3$  + Clover

Humic and fulvic acids from clover are decomposition products that possess mainly carboxyl functional groups (Kononava, 1961). Disassociation constants for humic acid are near pH 5.0 (Greenland, 1971) which is close to the acetic acid ( $\text{H}_4\text{C}_2\text{O}$ ) disassociation constant (4.75) (Weast, 1973). Titration of Orangeburg soil +  $\text{Fe}(\text{OH})_3$  with clover addition produced a ZPC at pH 4.70 with 0.01 and 0.1 M NaCl additions. Binding of soluble Al and Fe by carboxyl groups may have occurred.

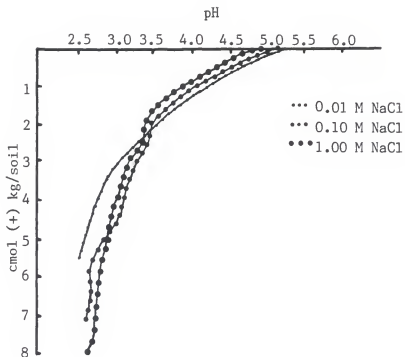


Fig. 4-29 Surface Properties of Orangeburg Topsoil +  $\text{Fe}(\text{OH})_3$  amended with 100 mg P/kg as Determined by Potentiometric Titration.

The 1.0 M NaCl plot did not intersect with other plots possibly due to mass action of Na replacing Al or Fe from the carboxyl group and producing acidity upon hydration, requiring less  $H^+$  from the titration. The ZPC values from previous plots were not at pH 4.70 indicating surface properties produced from clover application (Fig. 4-30). A second ZPC was produced at pH 3.8. Since organic functional groups bind covalently to iron minerals, partial reduction of kaolinite ZPC at pH 4.0 may have been produced by organic ligands binding to  $Fe(OH)_3$  on the kaolinite surface. Increased negative charge for  $H^+$  adsorption and reducing pH at the ZPC would result. With clover addition, positive charge was increased to 2.5 cmol (+)/kg compared to 1.0 and 2.0 cmol (+)/kg for Orangeburg +  $Fe(OH)_3$  and plus P addition, respectively.

#### Orangeburg + $Fe(OH)_3$ With P and Clover Addition

Addition of P and clover produced surface properties similar to clover addition alone. A ZPC value was obtained at pH 4.75 (Fig. 4-31) which is similar to carboxyl disassociation constants. If Al or Fe had been released into solution with increasing  $H^+$  additions, acidity from Al or Fe hydration could lower the ZPC of 1 M NaCl to pH 4.50. However, this pH may be an artifact of the titration from precipitation of

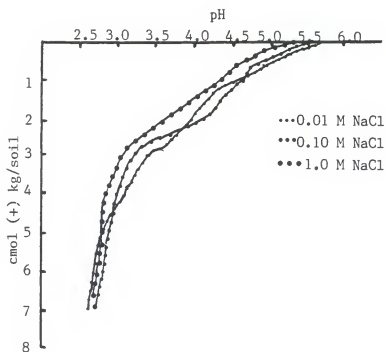


Fig. 4-30 Surface Properties of Orangeburg Topsoil +  $\text{Fe}(\text{OH})_3$  with 3.15 g/kg Applications as Determined by Potentiometric Titration.

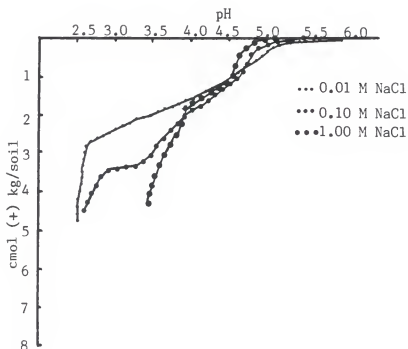


Fig. 4-31 Surface Properties of Orangeburg Topsoil + Fe(OH)<sub>3</sub> With 100 mg/kg P and 3.15 g/kg Clover Applications as Determined by Potentiometric Titration.

insoluble phosphates. A second ZPC of 3.5 with orthophosphate addition was not found. However a ZPC at pH 3.9 suggested presence of adsorption of P or organic components to  $\text{Fe}(\text{OH})_3$  surfaces.

Implications are that functional groups of clover bonded with Al and Fe ions in addition to adsorbing on Fe mineral surfaces. If this is the accurate mechanism, P would possess greater plant availability with clover addition. Results by yield, P uptake, and soil test methods such as Truog and Bray 2 extractable P indicate greater P availability with clover application. Surface properties confirm differences were produced by clover applications.

#### SEM Study

Orangeburg  $+\text{Fe}(\text{OH})_3$  + 100 mg P/kg soil with and without clover additions (3.15 g/kg) were placed on C coated Al stubs at varying clay concentrations. Samples containing 1600, 800, 533 and 320 mg clay/L were so concentrated to notice any difference between treatments. When samples were diluted to 160 mg clay/L in deionized water, differences in aggregation were observed. Greater clay dispersion (Fig. 4-32) without clover pretreatment was observed compared to increased aggregation with clover pretreatment (Fig. 4-33).

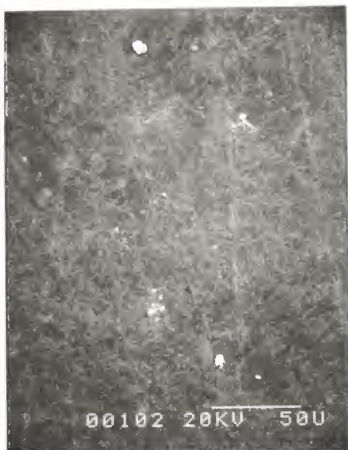


Fig. 4-32 Scanning Electron Micrograph (450X) of Orangeburg +  $\text{Fe}(\text{OH})_3$  Clay Fraction (160 mg clay/L) From the First Cropping Period.



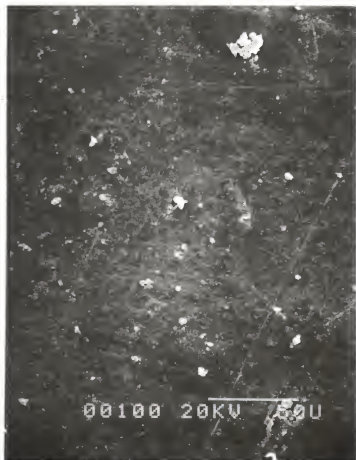


Fig. 4-33 Scanning Electron Micrograph (450X) of Orangeburg +  $\text{Fe}(\text{OH})_3$  Clay Fraction (160mg clay/L Amended With 3.15 g Clover/kg From the First Cropping Period.

Whether this relationship was produced from segregating clay fractions or existed previously in the soil is unknown. Much care was taken to isolate clay fractions with minimal reagent addition. A close up view of an aggregate magnified 10,000X, from a clover pretreatment sample is shown in Fig. 4-34. High molecular weight humic acids contain numerous functional groups (Inoue and Wada, 1968) which can bind to  $\text{Fe}(\text{OH})_3$  surfaces, thereby reducing soil surface area. (Schwertmann and Fisher, 1973). Clay fraction surface area could be reduced if aggregation of clay particles had occurred.

#### Conclusions

Incubation studies indicated that P fixation is reduced with clover pretreatment on soils containing sesquioxide minerals. Orangeburg topsoil + $\text{Fe}(\text{OH})_3$  and Orangeburg subsoil, coated with goethite, had lowered P fixation capabilities after receiving clover application. Increased P fixation capacity was observed on Orangeburg topsoil without  $\text{Fe}(\text{OH})_3$  application with increasing clover rates. At 60 d of incubation, P fixation capacity was reduced on all treatments after possible P mineralization of clover, and increase in pH reducing net positive charge on soil mineral surfaces. After 90 d, P fixation capacity had returned to near initial levels as pH decreased. Phosphorus fixation



Fig. 4-34 Scanning Electron Micrograph (10,000X)  
of an Aggregate From Orangeburg +  $\text{Fe}(\text{OH})_3$   
Clay Fraction Amended With 3.15 g Clover/kg  
From the First Cropping Period.

capacity of the Orangeburg soil without  $\text{Fe}(\text{OH})_3$  addition was probably produced by cation bridging of orthophosphate to organic functional groups. However, P fixation on  $\text{Fe}(\text{OH})_3$  treated soil and goethite in Orangeburg subsoil was reduced by organic anion specific adsorption. Crop production benefited from clover application. During the first two croppings of the glasshouse experiment, clover applications increased greater plant yield, P uptake, and extractable P levels. Without  $\text{Fe}(\text{OH})_3$  addition, cation bridging of P to organic components would have greater plant availability than a precipitation product of an insoluble Fe or Al phosphate as the soil pH decreased over time. With  $\text{Fe}(\text{OH})_3$  applications, complexation of soluble Fe and Al and/or organic ligand adsorption to  $\text{Fe}(\text{OH})_3$  surfaces may have increased yield, P uptake and extractable P levels. After refertilization of the third crop, P uptake for soil amended with clover was not significant according to treatment. However yield and extractable P levels increased with clover applications. Clover effectiveness in reducing P fixation persisted long after the time span for nutrient mineralization. Mechanisms of cation bridging and organic ligand adsorption appear to exist, confirmed data obtained from the surface charge and SEM study. Surface charge studies indicate a negative shift in ZPC values from P and clover applications, indicative of

ligand exchange reactions. Soil treatments with clover addition had ZPC values of 4.7, near pK values for carboxyl groups. The main functional group in humic acids from clover decomposition is carboxyl groups which can complex acid forming ions in the soil solution. Scanning electron microscopy appeared to show greater aggregation of the clay fraction with clover amendment, possibly indicating ligand exchange.

## CHAPTER V FERTILIZER COATING AND PLACEMENT EXPERIMENT

### Introduction

After application of water-soluble P fertilizer, P moves very slowly from the point of placement such that the orthophosphate is generally immobile in acid soils (Tisdale and Nelson, 1975). Distribution of fertilizer P, due to its immobility, is generally less than 1% of the total soil volume (Lindsay, 1959). Immobility of fertilizer P is due to rapid reaction with soil components and metastable precipitation products of diammonium phosphate (DAP), whose dissolution pH is 7.98, are dicalcium phosphate dihydrate (DCPD) and struvite ( $\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$ ) (Lindsay, 1959). Orthophosphate ions from the dissolution of fertilizer or solubilization of reaction products may form stable secondary products such as varisite, strengite, hydroxyapatite, or fluorapatite (Lindsay, 1979) or be specifically adsorbed on hydrous oxide mineral surfaces (Hingston et al., 1974).

Organic matter addition to soils which contain Fe and Al oxides has reduced net positive surface charge and orthophosphate adsorption in acidic environments (Moshi et al., 1974). Organic addition may also reduce solution Al (Bloom and McBride, 1979) or Fe activity

(Deb and Datta, 1967). Other observations produced evidence that organic functional groups bonded covalently to Fe mineral surfaces or ionically complexed Fe or Al solution species (Greenland, 1971).

Clover decompositional products contain high percentages of organic functional groups (Kononava, 1961) capable of reaction with sesquioxide minerals or dissolution products above pH 5 (Greenland, 1971). Studies of freshly humified clover adsorption to allophane (Inoue and Wanda, 1968) exhibited the effectiveness of organic adsorption to mineral surfaces.

The objective of the fertilizer coating experiment was to assess the effectiveness of coating granules of DAP with dried and ground clover as measured by dry matter production, P uptake, and extractable P levels.

#### Materials and Methods

##### Soil

An Orangeburg series topsoil + 5.6 g Fe as  $\text{Fe}(\text{OH})_3$  and subsoil corresponding to the Bt horizon as characterized in Tables 3-1 and 3-2 of Chapter 3 were used in the fertilizer coating experiment. Ferric hydroxide was prepared and applied by the same methodology described in Chapter 3. The soil was limed to pH 6.3 utilizing the liming curve developed in preliminary experimentation and incubated for 2 wk.

### Fertilizer Addition

Pots contained 2 kg of soil on a dry weight basis. The source of phosphate fertilizer applied was DAP with an application rate of 75 mg P/kg soil to all treatments. Variation in method of applications was the experimental treatment. Fertilizer was either completely mixed with the soil or applied by point placement. Point placement methodology consisted of placing one-half of the fertilizer rate (37.5 mg P/kg) at two positions spaced 4 cm from pot boundary along the diameter of the pot at a space of 6 cm. Depth of placement was 6 cm.

Clover-coated fertilizer granules were prepared by mixing small increments of Elmer's glue with dried and ground clover material until all material was bound together. Dried and ground clover was placed in a spherical paraffin mold with 37.5 mg P/kg as DAP placed in the center of the granule. Fertilizer granules were coated with 0.25, 0.50, 0.75 and 1.0 g of dried and ground clover with granule diameters ranging from 9 to 13 mm. Clover-coated granule placement in the soil was the same methodology as that of the point placement.

Uniform fertilizer addition included 150 mg N/kg soil as  $\text{NH}_4\text{NO}_3$ , 150 mg K/kg soil as KCl, and a secondary and micronutrient solution containing 19.8 mg Mg



as  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ , 11.4 mg Zn as  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ , 5.09 mg Cu as  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  and 1.2 mg B as  $\text{Na}_2\text{B}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$ . Fertilizer application was adjusted to a constant rate by treatment assuming 50% mineralization of clover nutrients.

#### Experimental Design

Eight fertilizer treatments applied to two soils and replicated three times were set in a randomized complete block (RCB) design. Fertilizer treatments were applied to Orangeburg subsoil and Orangeburg topsoil + 5.6 g Fe/kg as  $\text{Fe}(\text{OH})_3$ . Each soil received P fertilizer at a rate of 75 mg P/kg soil as DAP. Treatments were 1) Completely mixed soil without clover, 2) Completely mixed soil with 1.58 g clover/kg, 3) Completely mixed soil with 3.16 g clover/kg, 4) 2 granules coated with 0.25 g clover, 5) 2 granules coated with 0.50 g clover, 6) 2 granules coated with 0.75 g of clover, 7) 2 granules coated with 1.00 g clover, and 8) 2 point placements (uncoated DAP with same placement as granules.

Statistical analysis of the factorial experiment in RCB design data was performed utilizing the Statistical Analysis System. Mean separation was made using the single degree of freedom orthogonal contrast technique.

#### Methods

Two crops of maize were grown for 50 d to assess the initial and residual effectiveness of the

fertilizer treatments. Only top growth above the soil surface was analyzed during the first cropping period. The soil was not disturbed other than replanting the second crop. Soil and plant samples were analyzed after the second cropping period.

Plant samples were analyzed by previously described methods.

Soils were sampled after the second cropping period. Completely mixed soil samples were obtained as well as samples around the granules or point placement. Fertilizer residue was discarded but soil samples were taken up to 2 cm distance from point or granule placement. Bulk samples from granule or point placement treated soil, after soil near granules had been removed, were compared to completely mixed samples as well as soil 2 cm from granules.

Soil samples were analyzed for Truog and Bray 2 extractable P and pH.

## Results and Discussion

### Crop 1

Orangeburg subsoil contained 0.84% Fe as goethite coating clay mineral surfaces. Orangeburg topsoil was sandy containing Fe concretions with a citrate-dithionite-bicarbonate extraction concentration of 0.31% of the soil. Addition of amorphous  $\text{Fe}(\text{OH})_3$  (5.6 g/kg) to the topsoil increased the Fe content to a

total of 0.87%. Extractable Fe contents of both soils were equivalent, but as different mineral solid phases.

Phosphorus uptake by corn was affected by soil type and placement of fertilizer (Table 5-1). Greater P uptake was obtained with Orangeburg subsoil than topsoil +  $\text{Fe}(\text{OH})_3$  for the granule and point placement applications. This observation appears contradictory since from characterization data, the subsoil fixed 800 mg P/kg while the  $\text{Fe}(\text{OH})_3$  treated topsoil fixed only 640 mg P/kg. Goethite has less surface per unit weight than  $\text{Fe}(\text{OH})_3$  (Parfitt et al., 1975). Within the point placement and clover coated granule microsite, greater adsorptive surface would be available for P fixation on the  $\text{Fe}(\text{OH})_3$  treated soil since the fertilizer reacts with approximately 1% of total soil volume (Lindsay, 1959) resulting in greater P fixation by  $\text{Fe}(\text{OH})_3$  treated soil. Results are inconclusive for the completely mixed treatments. Unlike previous experimentation, time for decomposition of clover prior to fertilizer addition. Clover and fertilizers were applied on the same day. Lack of response to clover addition may be due to lack of time for decomposition before fertilizer addition. Fertilizer placement as a

Table 5-1. Soil and Treatment Effects on P Uptake From the First Cropping Period.

The First Cropping Period			
Treatment	Clover Applied	Orangeburg + Fe(OH) <sub>3</sub>	Orangeburg Subsoil
		P Uptake mg P/pot	
Completely Mixed (CM)	<u>g/kg</u>		
	0	9.63	11.97
	1.58	10.77	8.27
	3.15	11.87	10.97
Granule (G)	<u>g/granule</u>		
	1) 0.25	27.07	29.60
	2) 0.50	29.50	31.43
	3) 0.75	29.80	30.13
	4) 1.00	27.40	29.57
Point Placement (PP)	0	24.03	33.07
<hr/>			
Contrasts		-----p>F-----	
<hr/>			
Orangeburg + Fe(OH) <sub>3</sub> vs Orangeburg Subsoil		0.01	
CM vs PP		0.01	0.01
G vs PP		0.01	NS
G(3) vs G(1,2,4)		NS	NS
<hr/>			

granule or point placement exhibited greater superiority of P uptake and yield than complete mixing. Complete mixing of fertilizer to soil exposed a greater volume of soil to the fertilizer. Reduction in plant available fertilizer due to reaction with a greater volume of soil components reduced fertilizer effectiveness. Apparently, reduction in P uptake by corn due to complete mixing of the DAP was from reaction of fertilizer P with larger soil volumes.

No differences in P uptake effectiveness by individual granule treatments on either soil were observed, however, clover coated granules were superior in increasing P uptake to fertilizer point placement on the Orangeburg +  $\text{Fe}(\text{OH})_3$  treated soil. Theoretically, clover decompositional products should reduce positive charge near the granule microsite before dissolution of DAP, making the orthophosphate fraction more readily available for plant uptake. Also, dissolution pH of DAP (7.98) would depress Fe and Al activity as well as reduce pH-dependent positive charge near microsites.

Amorphous ferric hydroxide treated soil or goethite in the Orangeburg subsoil had no effect on the dry weight yield of the first corn crop. Treatment effects due to placement of 75 mg P/kg affected dry matter yield production. As shown in Table 5-2, granules and point placement were superior in dry weight yield production compared to complete mixing of

fertilizer with incremental clover additions. Treatment effects may be explained by enhanced P uptake due to placement of P fertilizer material. Lack of differences in yield on the two soils possibly indicates that the P rate of 75 mg/kg may have been too high. Since P uptake was different due to soils, it should follow that yield would be different by soil as it was by treatment. However, since P was not a limiting factor, optimal plant uptake of P across soils was obtained.

Calcium, Mg, and K uptake by corn followed closely to P treatment yield. Increased dry matter yield resulted in increased Ca, Mg, and K uptake but these elements in plant tissue were not interpreted as being deficient. Aluminum and Fe concentrations did not approach toxic levels in the plant during the first cropping period.

#### Crop 2

Soil pH values for both soils dropped from the limed pH values of 6.3 to the indigenous values of 4.7 and 5.2 (Table 5-3) for Orangeburg +  $\text{Fe}(\text{OH})_3$  and Orangeburg subsoil, respectively, over the two cropping periods. Although Al and Fe were never at toxic concentrations within the tissue, the percentage of P within tissue was lower (<0.1%) in Crop 2 than the first crop.

Table 5-2 Effect of Treatment on Maize Dry Matter  
Yield From the First Cropping Period.

<u>Treatment</u>	<u>Clover Applied</u>	<u>Yield g/pot</u>
Completely Mixed (CM)	<u>g/kg</u>	
	0	12.07
	1.58	12.05
	3.15	13.05
Granule (G)	<u>g/granule</u>	
	1) 0.25	21.97
	2) 0.50	22.82
	3) 0.75	22.77
	4) 1.00	21.50
Point Placement (PP)	0	21.42
<u>Contrasts</u>		<u>p&gt;F</u>
CM vs PP		0.01
G vs PP		NS
G (2) vs G(1,3,4)		NS

Decrease in pH increased sesquioxide ionic activity and reduced P availability. There was no apparent difference between pH of completely mixed soil and soil near granules or spot placement.

Truog extractable P levels of granule treatments were different with respect to soil. Greater concentrations of extractable P were found in the soil around granule placement with Orangeburg subsoil resulting in increased dry mater yield and P uptake than with Orangeburg topsoil +  $\text{Fe}(\text{OH})_3$  (Table 5-4). This observation confirmed the hypothesis that greater adsorptive surfaces would be available for P adsorption on the  $\text{Fe}(\text{OH})_3$  treated soil instead of goethite for granule and point placement.

Truog extractable P levels from soil near fertilizer granules were also affected by treatment (Table 5-5). There was no difference between extractable P levels from granule fertilizers or point placement resulting in lack of response in plant yield and P uptake for the two plant growth periods. The highest Truog extractable P results within granule treatments came from DAP granules coated with 0.50 g clover. However, yield was not increased comparatively to other granules or point placement treatments during either



Table 5-3 Effect of Soil and Fertilizer Placement on  
Soil pH. After the Second Cropping Period.

Treatment	pH	Contrast	p>F
<u>Completely Mixed</u>			
Orangeburg + Fe(OH) <sub>3</sub>	4.67	Topsoil vs Subsoil	0.01
Orangeburg Subsoil	5.24		
<u>Granule</u>			
Orangeburg + Fe(OH) <sub>3</sub>	4.68	Topsoil vs Subsoil	0.01
Orangeburg Subsoil	5.23		

Table 5-4. Truog Extractable P Levels on Granule  
Samples as Affected by Soil After the  
Second Cropping Period.

Treatment	Truog P levels	Contrast	p>F
mg/kg			
Orangeburg + Fe(OH) <sub>3</sub>	7.05	Topsoil vs Subsoil	0.05
Orangeburg subsoil	17.22		

cropping period. Phosphorus uptake from granule treatments was superior to point placement on Orangeburg + Fe soil during the first cropping. Soil around the granule or point placement possessed greater concentrations of Truog extractable P than soil from the completely mixed treatments. Completely mixing fertilizer with soil increases the volume of soil capable of reducing fertilizer availability. This trend was observed throughout the duration of the experiment. Truog extractable P levels by soil and treatment were indicative of plant yield and P uptake measurements since Truog levels denoted highly available P to plants.

Bray P 2 extractable P levels were affected by treatment and followed the same trends as the Truog extractable P results (Table 5-6). Completely mixed treatments were less effective than granule or point placement of fertilizer. There was no difference between granule or point placement methodologies. Granules coated with 0.5 g clover appeared more effective in supplying P than other granules manufactured.

Reduced P availability reduced plant yield by one-half if one compares the first to the second crop.

Table 5-5. Effect of Treatment on Granule Truog  
Extractable P Levels After the Second  
Cropping Period.

Treatment	Clover Applied	Truog P
Completely Mixed (CM)	<u>g/kg</u>	mg P/kg
	0	6.10
	1.58	5.98
	3.15	6.10
Granule (G)	<u>g/granule</u>	
	1) 0.25	10.28
	2) 0.50	25.60
	3) 0.75	19.63
	4) 1.00	18.08
Point Placement (PP)	0	24.85
<u>Contrast</u>		<u>p&gt;F</u>
CM vs PP		0.01
Gran vs PP		NS
Gran (2) vs Gran (1,3,4)		0.05

Table 5-6 Effect of Granule Treatments on Bray 2  
Extractable P Levels After the Second  
Cropping Period.

Treatment	Clover Applied	Bray 2 P
Completely Mixed (CM)	g/kg	mg P/kg
	0	20.58
	1.58	22.08
	3.15	19.50
Granule (G)	g/Gran	
	1) 0.25	38.37
	2) 0.25	63.48
	3) 0.75	52.63
	4) 1.00	47.65
Point Placement (PP)	0	60.60
Contrast		p>F
CM vs PP		0.01
Gran vs PP		NS
Gran (2) vs Gran (1,3,4)		0.05

Reduced P availability also induced a soil and treatment interaction in which the P in Orangeburg subsoil was more available to plants as determined by plant P uptake (Table 5-7) than P from Orangeburg topsoil +  $\text{Fe}(\text{OH})_3$ . Differences in P uptake produced a soil and treatment interaction in which yield was greater on Orangeburg subsoil than Orangeburg +  $\text{Fe}(\text{OH})_3$  treated soil (Table 5-8). Similar trends observed during the first cropping period occurred for the second cropping period. Point placement and granules were superior in producing yield and increasing P uptake to completely mixed placement methodologies. Loss of effectiveness of the 0.5 g clover coated granule in increasing P uptake on Orangeburg topsoil +  $\text{Fe}(\text{OH})_3$  was noted only during the second plant growth period.

### Conclusions

Point placement of fertilizer and clover coated granules were superior to completely mixing fertilizer and clover to the soil, as measured by corn yield, P uptake, Truog extractable P and Bray P 2 extractable levels of soil P. There was no difference in experimentation variables between point or granule placement of fertilizers except increased P uptake on Orangeburg topsoil +  $\text{Fe}(\text{OH})_3$  during the first cropping period. Lack of differences in yield between granule and point

Table 5-7 Soil and Treatment Effect on P uptake From the Second Cropping Period

the second cropping series			
Treatment	Clover Applied	Orangeburg + Fe(OH) <sub>3</sub>	Orangeburg Subsoil
		--- P uptake	mg/pot----
Completely Mixed (CM)	<u>g/kg</u>		
	0	2.17	2.88
	1.58	2.69	3.29
	3.15	2.40	3.20
Granule (G)	<u>g/granule</u>		
	1) 0.25	3.66	9.44
	2) 0.50	4.39	9.38
	3) 0.75	4.16	7.98
	4) 1.00	5.12	8.11
Point Placement (PP)	0	4.71	9.01
Contrasts		-----p>F-----	
Orangeburg + Fe(OH) <sub>3</sub> vs Orangeburg subsoil 0.01			
CM vs PP		0.01	0.01
G vs PP		NS	NS
G (2) vs G (1,3,4)		NS	-
G (1) vs G (2,3,4)		-	NS

Table 5-8. Soil and Treatment Effects on Yield from the Second Cropping Period.

Treatment	Clover Applied	Orangeburg + $\text{Fe}(\text{OH})_3$	Orangeburg Subsoil
		Yield g/Pot	
Completely Mixed(CM)	<u>g/kg</u>		
	0	2.67	3.60
	1.58	3.07	4.50
	3.15	3.27	4.27
Granule(G)	<u>g/granule</u>		
	1) 0.25	5.06	10.33
	2) 0.50	6.67	9.40
	3) 0.75	5.07	9.13
	4) 1.00	6.50	11.43
Point Placement(PP)	0	7.07	9.93
Contrasts		-----p>F-----	
Orangeburg + $\text{Fe}(\text{OH})_3$ vs Orangeburg Subsoil		0.01	0.01
CM vs PP		0.01	0.01
G vs PP		NS	NS
G(2) vs G(1,3,4)		NS	-
G(4) vs G (1,2,3)		-	NS

placements during this period may have been produced by the fertilizer rate of 75 mg P/kg soil as a concentrated point on the Orangeburg soil +  $\text{Fe}(\text{OH})_3$  resulting in sufficient P for plant growth.

Of the granules manufactured and applied, the 0.50 g clover coating rate produced the best results only on Orangeburg +  $\text{Fe}(\text{OH})_3$  treated soil, as measured by Truog and Bray P 2 extractable P levels. Possibly coating thickness was related to time of P release during microbial degradation which induced increased response to applied P. No difference between granule and point placement was observed on Orangeburg subsoil.

Differences between soils included pH, Truog extractable P levels, P uptake, and yield from the second cropping period. The pH of 4.7 of the Orangeburg topsoil +  $\text{Fe}(\text{OH})_3$  which would increase Al and Fe solution activity and increase net positive charge on Fe mineral surface reducing P availability. Reduction in P uptake and yield from the second cropping period are indicative of these types of changes. Changes over time were not as dramatic on Orangeburg subsoil. After liming and fertilizer P application, no differences in yield with respect to soils was observed during the first cropping period. However, as the two soils reverted to their natural status, a difference in yield with respect to soils was observed from a soil by treatment interactions during the second cropping



period. Truog P measured after the second cropping period was substantially lower in Orangeburg topsoil +  $\text{Fe}(\text{OH})_3$  than in the subsoil. Phosphorus deficiency in maize plants was also observed on the Orangeburg topsoil during the second cropping period.

Applications of P fertilizers to high-P fixing soils should be by band or point placement of fertilizer. If the sequioxide mineral in the soil possesses a high surface area, consideration to coating the P source material with an organic material may be favorable for increasing P uptake by a crop.

## CHAPTER VI SUMMARY AND CONCLUSIONS

Incubation study results indicate that P fixation is reduced with clover pretreatment on soils containing sesquioxide minerals. Orangeburg topsoil +  $\text{Fe}(\text{OH})_3$  and Orangeburg subsoil coated with goethite, had reduced P fixation capacities with increasing clover application rates. Increased amounts of P were fixed in Orangeburg topsoil without  $\text{Fe}(\text{OH})_3$  applications with increasing clover rates. At 60 d of incubation, P fixation capacity was reduced for all treatments. Possibly P mineralization from clover and pH increase reduced net positive charge on soil mineral surfaces. After 90 d, P fixation capacity had returned to near initial levels as soil pH decreased. Phosphorus fixation capacity by the Orangeburg soil without  $\text{Fe}(\text{OH})_3$  addition probably was produced by cation bridging of orthophosphate by organic functional groups. However, P fixation on  $\text{Fe}(\text{OH})_3$  treated soil and soil with goethite was reduced by organic adsorption mechanisms. Throughout the duration of the first glasshouse experiment, pretreatment with clover induced greater plant yield, increased P uptake except during the third cropping period, and extractable P levels. Dry weight yields averaged 350% higher with clover application than without clover

addition on  $\text{Fe}(\text{OH})_3$  treated soil. Soil  $\text{Fe}(\text{OH})_3$  remained in an amorphous state throughout the 180 d of cropping. Without  $\text{Fe}(\text{OH})_3$  addition, cation bridging of P to organic functional groups would have resulted in greater plant P availability than a precipitation product of an insoluble Fe or Al phosphate. With  $\text{Fe}(\text{OH})_3$  application, complexation of solution Fe and Al and/or organic ligand coordination to  $\text{Fe}(\text{OH})_3$  surfaces may have effectively increased plant yield, P uptake, and extractable P levels. After P refertilization of the third crop, P uptake across clover levels was not significant according to treatment, but yield and extractable P levels increased with clover rate of application. Clover effectiveness in reducing P fixation remained long after clover nutrients were mineralized. Mechanisms of ionic complexations by organic functional groups and organic ligand adsorption appear to exist from data obtained from the surface charge. Surface charge studies indicate a negative shift in ZPC values with P and clover application, indicative of ligand exchange reactions. Carboxyl groups can complex acid forming ions from soil solutions. Scanning electron microscopy appears to reveal a greater aggregation of the clay fractions with clover amendment.

A second glasshouse experiment was conducted to determine effectiveness of coating DAP with clover. If complete mixing of clover with the soil induced a

positive response in lowering P fixation, clover amendments should reduce P fixation around P fertilizer microsites. Point placement of fertilizer and clover-coated granules were superior to completely mixing fertilizer and clover into the soil, as measured by dry matter yield, P uptake, and extractable P levels. Clover granules were somewhat superior to point placement in increasing P uptake on Orangeburg +  $\text{Fe}(\text{OH})_3$  during initial cropping. Of the granules manufactured, the 0.5 g-clover coating produced the best results of extractable P levels on Orangeburg +  $\text{Fe}(\text{OH})_3$  treated soil.

When management is considering practices for crop production on highly-weathered acidic soils possessing Fe mineral coatings, management practices using an organic material such as a legume residue to be incorporated into the soil should be considered because increases in crop production with minimal input and less fertilizer costs may be obtained. In the near future, organic coatings of P fertilizer material may increase yields on highly weathered soils. Research reported herein tried to bridge the gap between laboratory results and plant growth studies. It appeared that theories developed from laboratory results would explain effectiveness of fertilizer for plant growth with clover application.

## BIBLIOGRAPHY

- Appelt, H., N. T. Coleman, and P. F. Pratt. 1975a. Interactions between organic compounds, minerals and ions in volcanic ash derived soils: I. Adsorption of benzoate, p-OH benzoate, salicylate, and phthalate ions. *Soil Sci. Am. Proc.* 39:623-627.
- Appelt, H., N. T. Coleman, and P. F. Pratt. 1975b. Interactions between organic compounds, minerals and ions in volcanic ash derived soils: II. Effects of organic compounds on the adsorption of phosphate. *Soil Sci. Am. Proc.* 39:628-630.
- Atkinson, R. J., A. M. Posner, and J. P. Quirk. 1972. Kinetics of heterogenous isotopic exchange reactions. Exchange of phosphate at the alpha-FeOOH aqueous solution interface. *J. Inorg. Nucl. Chem.* 34:2201-2211.
- Ballard, R. 1974. Extractability of reference phosphates by soil test reagents in absence and presence of soils. *Soil and Crop Sci. Soc. Fla. Proc.* 33:169-174.
- Bhat, K. K. S., and S. Bouyer. 1968. Effect of organic matter on the isotopically exchangeable phosphorus on some types of tropical soils. p. 299-313. *In* Isotopes and Radiation in Soil Organic-Matter Studies. Proc. Symp. IAEA/FAO, Vienna. 1968.
- Bloom, P. R. 1979. Titration behavior of aluminum organic matter. *Soil Sci. Soc. Am. J.* 43:815-817.
- Bloom, P. R. 1981. Phosphorus adsorption by an aluminum peat complex. *Soil Sci. Soc. Am. J.* 45:267-272.
- Bloom, P. R., and M. B. McBride. 1979. Metal ion binding and exchange with hydrogen ions in acid washed peat. *Soil Sci. Soc. Am. J.* 43:687-692.
- Bohn, H. L., B. L. McNeal, and G. A. O'Connor. 1985. *Soil Chemistry*. John Wiley and Sons, New York.

- Carroll, D. 1958. Role of clay minerals in the transportation of iron. *Geochemica et Cosmochimica Acta*, 14:1-28.
- Chapman, H. D. 1965. Total exchangeable bases. p 902-904. In *Methods of Soil Analysis*, Part 1. Am. Soc. Ag., Inc., Madison, WI.
- Chen, Y., N. Senesi, and M. Schnitzer. 1977. Information provided on humic substances by E4/E6 ratios. *Soil Sci. Soc. Am. J.* 41:352-358.
- Chu, C. R., W. W. Moschler, and G. W. Thomas. 1962. Rock phosphate transformations in acid soils. *Soil Sci. Soc. Am. J.* 26:476-478.
- Datta, N. P., and N. N. Goswami. 1962. Transformations of organic matter in relation to the availability of nutrients to plants. p 223-238. In *Isotopes and Radiation in Soil Organic Matter Studies*. Proc. Symp. IAEA/FAO, Vienna.
- Datta, N. P., and B. R. Nagar. 1968. Studies on the decomposition of organic matter in soil in relation to its maintenance and the availability of nutrients to plants, and on the origin and structure of humic acids. p 287-296. In *Isotopes and Radiation in Soil Organic-Matter Studies*. Proc. Symp. IAEA/FAO, Vienna.
- Day, P. R. 1965. Particle fractionation and particle size analysis. P 532-543. In *Methods of Soil Analysis*. Part 1. Am. Soc. Ag., Inc., Madison, WI.
- Deb, D. L., and N. P. Datta. 1967. Effect of associating anions on phosphorus retention in soil: II. Under variable anion concentration. *Plant Soil* 26(3):432-444.
- Dixon, J. B. 1977. Kaolinite and serpentine minerals. p 357-398. In *Minerals in Soil Environments*. SSSA. Madison, WI.
- Easterwood, G. W. 1982. Liming effect of carbonate apatites. Master's thesis. University of Florida.
- Evans, L. T., and E. W. Russell. 1959. The adsorption of humic and fulvic acids by clays. *J. Soil Sci.* 10(1):119-132.

- Fassbender, H. W., and Y. K. Igue. 1967. Comparacion de metodos radiometricos y colorimetricos en estudios sobre retencion y transformacion de fosfatos en suelo. *Turialba* 17:284-287.
- Follett, E. A. C. 1965. The retention of amorphous colloidal ferric hydroxide by kaolinites. *J. Soil Sci.* 16:334-341.
- Fox, R. L., and E. J. Kamprath. 1970. Phosphate sorption isotherms for evaluating the phosphate requirements of soils. *Soil Sci. Soc. Am. Proc.* 34:902-907.
- Greenland, D. J. 1965. Interactions between clays and organic compounds in soils. Part II. Adsorption of soil organic compounds and its effect on soil properties. *Soils Fert.* 28:521-531.
- Greenland, D. J. 1971. Interactions between humic and fulvic acids and clays. *Soil Sci.* 111(1):34-41.
- Hammond, L. L. 1978. Agronomic measurements of phosphate rock effectiveness. p 147-173. In International Fertilizer Development Center, Seminar on Phosphate Rock for Direct Application, Muscle Shoals, Ala.
- Hashimoto, Y., and H. Takayama. 1971. Inhibiting effect of nitrohumates and on phosphorus fixation in soil. VII. Inhibiting effect using synthesized iron compounds as the fixation materials. *J. Sci. Soil* 42(1):37-43.
- Hinga, G. 1973. Phosphate sorption capacity in relation to properties of several types of Kenya soil. *East Afr. Agri. For. J.* 38:400-404.
- Hingston, F. J., A. M. Posner, and J. P. Quirk. 1974. Anion adsorption by goethite and gibbsite. II. Desorptions of anions from hydrous oxide surfaces. *J. Soil Sci.* 25(1):16-26.
- Hoagland, D. R., and D. I. Arnon. 1938. Growing plants without soil by the water-culture method. Univ. of Cal. Ag. Exp. Ssta. Berkeley, CA. Circular 347.
- Hsu, P. H. 1965. Fixation of phosphate by aluminum and iron in acidic soils. *Soil Sci.* 99(6):398-402.
- Inoue, T., and K. Wada. 1968. Adsorption of humified clover extracts by various clays. *Trans. 9th Int. Congr. Soil Sci., Adelaide*, 3:289-298.

- Kamprath, E. J. 1967. Residual effects of large applications of phosphorus on high fixing soils. *Agron. J.* 59:25-27.
- Kittrick, J. A. 1977. Mineral equilibria and the soil system. p 1-24. In Minerals in Soil Environments. Soil Sci Soc Am., Inc. Madison, WI.
- Kononova, M. M. 1966. Soil Organic Matter. 2nd Edition Pergamon Press, Oxford.
- Kunze, E. W. 1965. Pretreatment for Mineralogical Analysis. p 574-576. In Methods of Soil Analysis, Part 1. American Society of Agronomy, Inc., Madison, WI.
- Laverdiere, M. R., and R. M. Weaver. 1977. Charge characteristics of spodic horizons. *Soil Sci. Soc. Am. J.* 41:505-510.
- Lehr, J. R., and G. H. McClellan. 1972. A laboratory scale for evaluating phosphate rocks for direct applications. *TVA Bull.* Y-43.
- Levashkevich, G. A. 1966. Interactions of humic acid with iron and aluminum hydroxides. *Soviet Soil Sci.* 4:422-427.
- Lindsay, W. L. 1959. Behavior of water soluble phosphate. In Proc. Tenth Annual Fertilizer Conference in the Pacific Northwest. Tacoma, WA.
- Lindsay, W. L. 1979. Chemical Equilibria in Soils. John Wiley and Sons, New York.
- Lindsay, W. L., and E. C. Moreno. 1960. Phosphate phase equilibria in soils. *Soil. Sci. Soc. Am. Proc.* 24:177-182.
- Lockett, J. L. 1938. Nitrogen and phosphorus changes in the decomposition of rye and clover at different stages of growth. *Soil Sci.* 45:13-24.
- Manojlevic, S. 1965. Study of the role of humic acid in the fixation of soluble phosphorus in soil. *Soil Fert.* 29:37-41.
- Martell, A. E., and M. Calvin. 1952. Chemistry of the Metal Chelate Compounds. Prentice-Hall, Englewood Cliffs, NJ..



- McLean, E. O. 1982. Soil pH and lime requirement. p 199-224. In Methods of Soil Analysis. Part 2. Am. Soc. Agron., Inc., Madison, WI.
- Mendez, J., and E. J. Kamprath. 1978. Liming of Latosols and the effect on P response. Soil Sci. Soc. Am. J. 41:86-88.
- Moshi, A. O., A. Wild, and D. J. Greenland. 1974. Effect of organic matter on the charge and phosphate adsorption characteristics of Kikuyu red clay from Kenya. Geoderma 11:275-285.
- Murphy, J., and J. P. Riley. 1962. A modified solution method for determination of phosphate in natural waters. Anal. Chim. Acta 27:31-36.
- Nagarajah, S., A. M. Posner, and J. P. Quirk. 1970. Competitive adsorption of phosphate with polyglacturonate and other organic anions and oxide surfaces. Nature 228:83-84.
- Parfitt, R. L., R. J. Atkinson, and R. St. C. Smart. 1975. The mechanism of phosphate fixation by iron oxides. Soil Sci. Soc. Am. Proc. 39:837-841.
- Parfitt, R. L., A. R. Fraser, and V. C. Farmer. 1977. Adsorption in hydrous oxides. III. Fulvic acid and humic acid on goethite, gibbsite and imogolite. J. Soil Sci. 28:289-296.
- Parfitt, R. L., and J. D. Russell. 1977. Adsorption of hydrous oxides. IV. Mechanisms of adsorption of various ions on goethite. J. Soil Sci. 28:297-305.
- Parks, G. A., and P. L. de Bruyn. 1962. The zero point of charge of oxides. J. Phys. Chem. 66:967-973.
- Roy, A. C., M. Y. Ali, R. L. Fox, and J. A. Silva. 1971. Influence of calcium silicate on phosphate solubility and availability in Hawaiian Latosols. Proc. Int. Symp. Soil Fert. Eval. (New Delhi) 1:757-765.
- Ryden, J. C., J. R. McLaughlin, and J. K. Syers. 1977. Time-dependent sorption of phosphate by soils and hydrous ferric oxides. J. Soil Sci. 28:585-595.
- Sanchez, P. A., and G. Uehara. 1980. Management considerations for acid. In The Role of Phosphorus in Agriculture. ASA, CSSA, and SSA. Madison, WI.

- Schwertmann, U. 1959. Mineralogische und chemische untersuchungen an eisenoxyden in boden und sedimenten. Neues Jb. Miner. Abk. 93:67-86.
- Schwertmann, U. 1966. Inhibitory effect of soil organic matter on the crystallization of amorphous ferric hydroxide. Nature. 212:645-646.
- Schwertmann, U., and W. R. Fisher. 1973. Natural amorphous ferric hydroxide. Geoderma 10:237-247.
- Schwertmann, U., and R. M. Taylor. 1977. Iron oxides. p 145-181. In Minerals in Soil Environments. SSSA. Madison, WI.
- Silva, J. A. 1971. Possible mechanisms for crop response to silicate applications. Proc. Int. Symp. Soil Fert. Eval. (New Delhi) 1:805-814.
- Singh, B. B., and J. P. Jones. 1976. Phosphorus sorption and desorption characteristics of soil as affected by organic residues. Soil Sci. Soc. Am. J. 40:389-394.
- Stevenson, F. J. 1982. Humus Chemistry. John Wiley and Sons, NY.
- Stoop, W. A. 1974. Interactions between phosphate adsorption and cation adsorption by soils and implications for plant nutrition. PhD. Thesis. Univ of Hawaii, Honolulu. 203 p. (Diss. Abstr. 75-5042) University Microfilms, Ann Arbor, Michigan.
- Struthers, P. H., and D. H. Sieling. 1950. Effect of organic anions in phosphate precipitation by iron and aluminum as influenced by pH. Soil Sci. 69:205-213.
- Taylor, R. M., and U. Schwertmann. 1974. The association of phosphorus with iron in ferruginous soil concretions. Aust. J. Soil Res. 12:133-145.
- Tisdale, S. L., and W. L. Nelson. 1975. Soil Fertility and Fertilizers. Third Edition. Macmillan Publishing Company, NY.
- Trong, B., R. Bertrand, S. Burdin, and J. Pichot. 1974. Contribution a l'etude du phosphore dan les sols derives de roches volcaniques de l'elle de la Reunion (Mascaregnes). Action due carbonate et du silicate de calcium. Agron. Trop. (France) 29:663-674.

- Walkley, A., and I. A. Black. 1934. An examination of the Degtjareff method for determining soil organic matter and a proposed modification of the chromic acid titration method. *Soil Sci.* 37:3=29-38.
- Wann, S. S., and G. Uehara. 1978. Surface charge manipulation of constant surface potential soil colloids: I. Relation to sorbed phosphorus. *Soil Sci. Soc. Am. J.* 42:565-570.
- Weast, R. C. 1973. *Handbook of Chemistry and Physics*. CRC Press, Cleveland, OH.
- Woodruff, J. R., and E. J. Kamprath. 1965. Phosphorus adsorption maximum as measured by the Langmuir isotherm and its relationship to phosphorus availability. *Soil Sci. Soc. Am. Proc.* 29:148-150.
- Yost, R. S., E. J. Kamprath, E. Lobato, and G. C. Naderman, Jr. 1979. Phosphorus response of corn on an Oxisol as influenced by rates of placement. *Soil Sci. Soc. Am. J.* 43:388-343.
- Yuan, T. L. 1980. Adsorption of phosphate and water extractable soil organic material by synthetic aluminum silicates and acid soils. *Soil Sci. Soc. Am. J.* 44:951-955.
- Zunino, H., and J. P. Martin. 1977. Metal-binding organic macromolecules in soil: 1. Hypothesis interpreting the role of soil organic matter in the translocation of metal ions from rocks to biological systems. *Soil Sci.* 123(2):65-76.

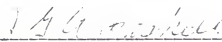
#### BIOGRAPHICAL SKETCH

George William Easterwood was born on April 8, 1955, in Sheffield, Alabama. He was reared in a rural area whose economy was based largely on agriculture. He attended and graduated from Cherokee Vocational High School in Cherokee, Alabama, in 1973. He then attended the University of North Alabama where he obtained a B.S. degree in zoology with a minor in chemistry in 1977. After graduation, he was employed at the International Fertilizer Development Center (IFDC) in Muscle Shoals, Alabama, for 3 years. During this period, he developed an interest in agricultural research and entered the University of Florida in 1980 under the directorship of Dr. J. J. Street. After graduation with a master's degree in 1982, he returned to IFDC for a year. In 1984, he returned to the University of Florida to pursue a Ph.D. degree in soil science under the directorship of Dr. J. B. Sartain.

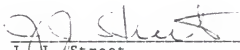
I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

  
J. B. Sartain, Chairman  
Professor of Soil Science

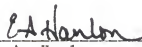
I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

  
J. G. A. Fiskell  
Professor of Soil Science

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

  
J. V. Street  
Associate Professor of Soil Science

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

  
E. A. Hanlon  
Assistant Professor of Soil Science

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.



---

W. G. Harris  
Assistant Professor of Soil  
Science

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

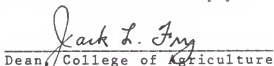


---

S. H. West  
Professor of Agronomy

This dissertation was submitted to the Graduate Faculty of the College of Agriculture and to the Graduate School and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

August, 1987

---

Dean, College of Agriculture

---

Dean, Graduate School